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(Signed) Md. Jasimuzzaman

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THE PARTIAL OXIDATION OF n-BUTANE IN HOMOGENEOUS AND TRANSPORTED BED REACTORS

BY

MD. JASIMUZZAMAN

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

EDMONTON, ALBERTA
SPRING, 1972

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE PARTIAL OXIDATION OF n-BUTANE IN HOMOGENEOUS AND TRANSPORTED BED REACTORS submitted by MD. JASIMUZZAMAN in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Experimental investigations of the partial oxidation of n-butane with air were carried out in homogeneous and transported bed reactors. The effects of the inlet temperature and the inlet hydrocarbon to oxygen ratio were studied in the homogeneous reactor. The inlet temperature affected the induction period, but the overall distribution of the products remained relatively unaltered. The hydrocarbon to oxygen ratio affected the temperature rise and the product selectivity, higher ratios leading to lower temperature rise and better selectivity in the reactor.

Simplified kinetic schemes were proposed to describe the reaction and the parameters of two such models were estimated by a numerical method using the data for conversion and temperature. The two models were tested using them to predict the temperature profiles and conversions for a number of independent runs made earlier in this laboratory.

Solid particles in a transported bed reactor take up the heat of reaction and reduce the temperature rise in the reactor. Solution of a theoretical model for a transported bed reactor revealed that the radial variation in temperature of solid particles 50 to 800 microns in diameter is insignificant. The homogeneous reactor used in the present study was provided with solids feed, heating and separation systems in order that it can be used as a transported bed reactor. Experimental runs were carried out in this reactor in a relatively narrow range of solids to gas loading ratios between 3 and 5. The selectivities to different products were compared to those in the homogeneous reactor. A significant increase in the selectivity to oxygenated products was achieved. For runs carried out under similar conditions, the selectivity to oxygenated products rose from 0.30 in the homogeneous reactor to 0.50 lb-mole/lb-mole n-butane reacted in the transported bed reactor. For the range of operating conditions in the present study, no effect of surface was observed and the kinetic models proposed for the homogeneous reactor could be used to predict the overall conversions and temperature profiles in the transported bed reactor.

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CHAPTER I

INTRODUCTION

The slow gas phase partial oxidation of hydrocarbons takes place by degenerate chain branching and results in the formation of a large number of products such as olefins, alcohols, aldehydes, ketones, and lower paraffins. The reaction is often an economic route for the production of the oxygenated compounds. Since these products are more expensive than the parent hydrocarbons, there is an economic incentive for the process. The reaction has also been used in recent years to obtain unsaturates from the paraffins.

A large volume of work on the partial oxidation reactions has been reported in the literature over the past seventy years. However, the complexity of the reaction has frustrated efforts at establishing a mechanism for the reaction, and contradictory results are reported on the effects of different variables. The selectivity of the reaction is poor and though the economy of an industrial process must depend on improved selectivity, published information on this aspect is scarce.

An important variable in hydrocarbon oxidation is the temperature of the reaction system. In an adiabatic plug flow reactor, the reaction starts with an induction period followed by a very rapid rise in the reaction rate and in the temperature of the reacting stream, due to the evolution of a large amount of heat. This rise in temperature causes a decrease in selectivity by changing the course of the reaction and/or by further oxidation of the desirable components at the elevated temperatures.

In a transported bed reactor, inert solid particles are carried with the gas to take up the heat of reaction and hence control the rise in temperature. By a suitable choice of variables, it is likely to be possible to obtain an almost isothermal operation, or even to obtain a prescribed optimum temperature profile in the reactor. This would improve the selectivity and hence the economy of the process.

A number of studies have been carried out in the University of Alberta on the partial oxidation of n-butane in the last two decades. More recently, in 1966, Anderson (1) built a reactor with multiple sampling points and temperature probes along the length of the reactor. This reactor was modified in the present investigation to operate both as a homogeneous reactor and as a transported bed reactor. Experimental investigations were carried out in the homogeneous reactor to study the effect of inlet temperatures and inlet n-butane to oxygen ratios on the overall oxidation process and on the product distribution.

Selectivity in the transported bed was investigated and compared with the results from homogeneous runs. Mathematical models for the reactors were formulated based on the postulation of certain kinetic schemes for the reaction.

CHAPTER II

LITERATURE REVIEW

2.1 INTRODUCTION

The main research interest in the partial oxidation of hydrocarbons is due to its industrial importance. In chemical industries, a wide variety of hydrocarbons from petroleum stock are allowed to undergo incomplete combustion, leading to the derivation of all kinds of intermediate products in heavy organic synthesis. The choice of optimum conditions for the partial combustion process is very important, since both the yield of the valuable products and the capital investment for the industrial application of the process depend on this choice.

The knowledge of the mechanism of the reaction would make the choice relatively easy, but the mechanism is very complex and is not yet known. Hence, research in hydrocarbon oxidation almost always had two objectives in view: to elucidate the mechanism of the reaction and to search for the optimum reaction conditions. In the following sections, present status of knowledge in these two areas is reviewed.

2.2 MECHANISM

The vapour phase partial oxidation of paraffins is a free radical reaction with degenerate chain branching. The basic experimental facts concerning the hydrocarbon oxidation are relatively well established. However, the detailed nature of the complicated series and parallel steps leading to the formation of a host of intermediate and end products is far from being understood.

The initiation reaction is today almost universally accepted to be a reaction between a paraffin (shown henceforth as _n_-butane) and an oxygen molecule (2). The reaction normally takes place in the gas phase with an activation energy of 40-50 kcal/mole and with an equal amount of endothermic heat of reaction. This initiation leads to the formation of a butyl radical and a hydroperoxy radical. The C-H bond in the CH_2 group of n-butane is 2-3 kcal less than that in the CH_3 group and hence the amount of iso-butyl radical formed will be larger than the n-butyl radical. This effect will be more pronounced at lower temperatures, when a small difference in the activation energy can direct the course of the reaction.

$$CH_3CH_2CH_2CH_3 + O_2 \rightarrow CH_3CH_2CH_2\dot{C}H_2 + H\dot{O}_2 \qquad (2.1)$$

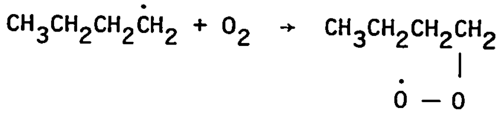
$$CH_3CH_2CH_2CH_3 + O_2 \rightarrow CH_3CH_2\dot{C}HCH_3 + H\dot{O}_2 \qquad (2.2)$$

The initiation reaction is followed by a complex series of propagating steps. The butyl radical formed can react either with an oxygen molecule forming olefin as proposed for propane by Lewis and von Elbe (4) and later supported by several authors (5,6):

$$CH_3CH_2CH_2\dot{C}H_2 + O_2 \rightarrow CH_3CH_2CH = CH_2 + H\dot{O}_2 \qquad (2.3)$$

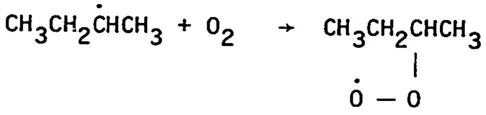
$$CH_3CH_2\dot{C}HCH_3 + O_2 \rightarrow CH_3CH = CHCH_3 + H\dot{O}_2 \qquad (2.4)$$

or it can combine with oxygen forming a butyl peroxide radical as suggested, among others, by Hinshelwood (7).



$$CH_3CH_2CH_2\dot{C}H_2 + O_2 \rightarrow CH_3CH_2CH_2\underset{\dot{O}-O}{\underset{|}{CH_2}}$$

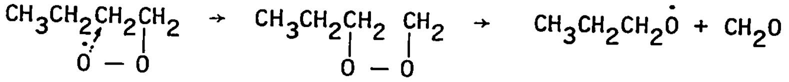
(2.5)



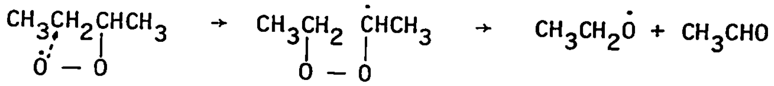
$$CH_3CH_2\dot{C}HCH_3 + O_2 \rightarrow CH_3CH_2\underset{\dot{O}-O}{\underset{|}{CH}}CH_3$$

(2.6)

Semenov (2,3) and Shtern (8) developed a mechanism based on the isomerization of the peroxy radicals formed as above. The oxygen atom bearing the free valence of the peroxide radical can attack a C-C bond in the radical itself leading to isomerization and subsequent decomposition:



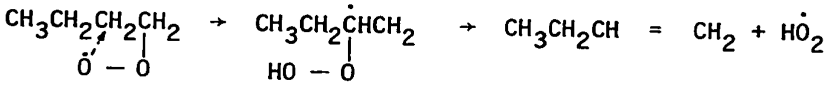
$$\underset{\dot{O}\;-\;O}{CH_3CH_2CH_2CH_2} \rightarrow \underset{O\;-\;O}{CH_3CH_2CH_2\;CH_2} \rightarrow CH_3CH_2CH_2\dot{O} + CH_2O \qquad (2.7)$$



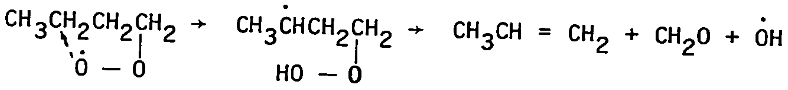
$$\underset{\dot{O}\;-\;O}{CH_3CH_2CHCH_3} \rightarrow \underset{O\;-\;O}{CH_3CH_2\;\dot{C}HCH_3} \rightarrow CH_3CH_2\dot{O} + CH_3CHO \qquad (2.8)$$

This method of isomerization first proposed by Shtern involves the rupture of a C-C bond and the formation of a C-O bond, and is thermoneutral. The second step, the break up of the isomerized radical is exothermic since a C = O bond (75 kcal) is made at the expense of an O-O bond (40 - 50 kcal). The activation energy of this step is probably low and isomerization is the rate determining step. Semenov obtained a value of 20 kcal/mole for the activation energy.

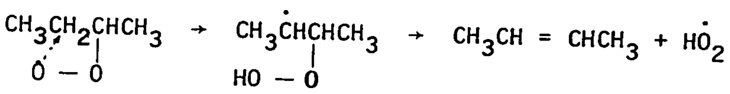
Another type of isomerization suggested by Semenov is the migration of a hydrogen atom from the carbon atom to the oxygen atom, with rupture of a C-H bond (95 kcal) and formation of an O-H bond (103 kcal), followed by decomposition.



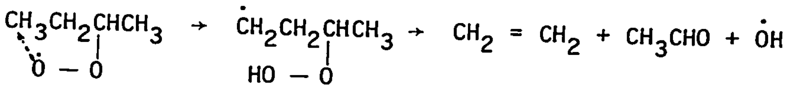
$$\underset{\dot{O}\;-\;O}{CH_3CH_2CH_2CH_2} \rightarrow \underset{HO\;-\;O}{CH_3CH_2\dot{C}HCH_2} \rightarrow CH_3CH_2CH = CH_2 + H\dot{O}_2 \qquad (2.9)$$



$$\underset{\dot{O}\,-\,O}{CH_3CH_2CH_2CH_2} \rightarrow \underset{HO\,-\,O}{CH_3\dot{C}HCH_2CH_2} \rightarrow CH_3CH = CH_2 + CH_2O + \dot{O}H \qquad (2.10)$$



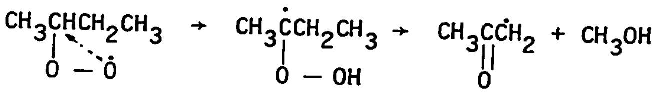
$$\underset{\dot{O}\,-\,O}{CH_3CH_2CHCH_3} \rightarrow \underset{HO\,-\,O}{CH_3\dot{C}HCHCH_3} \rightarrow CH_3CH = CHCH_3 + H\dot{O}_2 \qquad (2.11)$$



$$\underset{\dot{O}\,-\,O}{CH_3CH_2CHCH_3} \rightarrow \underset{HO\,-\,O}{\dot{C}H_2CH_2CHCH_3} \rightarrow CH_2 = CH_2 + CH_3CHO + \dot{O}H \qquad (2.12)$$

Reaction (2.12) will be highly endothermic because it involves the rupture of a C-O bond (75 kcal) and formation of a C=C bond (57 kcal) and a C=O bond (75 kcal). Isomerization will again be the rate determining step and the activation energy in this case has been calculated to be higher than in isomerization with attack on C-C bond.

In addition to this, there can be an isomerization involving the rupture of both the C-C bond (75 kcal) and the C-H bond (95 kcal) with the formation of a C-O bond (75 kcal) and an O-H bond (103 kcal).



$$\underset{O\,-\,\dot{O}}{CH_3CHCH_2CH_3} \rightarrow \underset{O\,-\,OH}{CH_3\dot{C}CH_2CH_3} \rightarrow \underset{O}{\overset{}{CH_3C}}\dot{C}H_2 + CH_3OH \qquad (2.13)$$

A large number of further reactions of the intermediates and the free radicals follow. But meanwhile, the number of radicals in the reacting system must multiply in order to give the reaction its autocatalytic nature. Two possible routes are suggested:

$$RCHO + O_2 \rightarrow R\dot{C}O + H\dot{O}_2 \qquad (2.14)$$

Alternatively, the alkyl peroxy radical formed by reactions (2.5) and (2.6) can react with an alkane forming a hydroperoxide, which can decompose into two free radicals:

$$\dot{R}O_2 + RH \rightarrow ROOH + \dot{R} \tag{2.15}$$

$$ROOH \rightarrow R\dot{O} + \dot{O}H \tag{2.16}$$

Experimental evidence for each of these branching processes has been advanced, but it is possible that both these processes take place in a reaction system.

Each of the branching process results in a net increase of two free radicals. The reaction thus starts slowly with an induction period during which time only small amounts of the paraffin and oxygen react. Finally, sufficiently high amounts of branching agents are obtained leading to the formation of a large amount of free radicals and resulting in a rapid rise in the rate of the reaction. The reaction is highly exothermic and in an adiabatic reactor, the rise in rate is accompanied by a sharp rise in temperature of the reacting mixture.

The number of free radicals in the system eventually drops to zero because of termination reactions. The termination can occur by recombination of radicals, reaction leading to nonreactive products, or by contact with the surface.

The different radicals formed in the system can react in a variety of ways. The alkoxy radicals formed can decompose or react with oxygen or hydrocarbon molecules as follows:

$$CH_3CH_2CH_2\dot{O} \rightarrow CH_3\dot{C}H_2 + CH_2O \tag{2.17}$$

$$CH_3CH_2\dot{O} \rightarrow \dot{C}H_3 + CH_2O \tag{2.18}$$

$$CH_3CH_2\dot{O} \rightarrow CH_3CHO + \dot{H} \tag{2.19}$$

$$CH_3CH_2\dot{O} + C_4H_{10} \rightarrow CH_3CH_2OH + \dot{C}_4H_9 \tag{2.20}$$

$$CH_3\dot{O} \rightarrow CH_2O + \dot{H} \tag{2.21}$$

$$CH_3\dot{O} + C_4H_{10} \rightarrow CH_3OH + \dot{C}_4H_9 \tag{2.22}$$

$$CH_3\dot{O} + O_2 \rightarrow CO + H_2O + \dot{O}H \tag{2.23}$$

For alkoxy radicals higher than the methoxy radicals, the decomposition reaction is likely to predominate.

The lower alkyl radicals formed can react with an alkane molecule forming the lower paraffins. The hydrogen radical also can react in a similar fashion.

$$\dot{H} + C_4H_{10} \rightarrow H_2 + \dot{C}_4H_9 \tag{2.24}$$

$$\dot{C}H_3 + C_4H_{10} \rightarrow CH_4 + \dot{C}_4H_9 \tag{2.25}$$

$$CH_3\dot{C}H_2 + C_4H_{10} \rightarrow CH_3CH_3 + \dot{C}_4H_9 \tag{2.26}$$

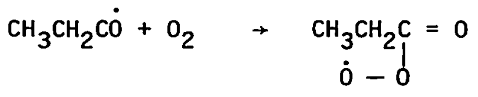
The acyl radicals formed by the oxidation of aldehydes in the branching reaction can react in a number of ways. They can decompose as follows:

$$CH_3CH_2C\dot{O} \rightarrow CH_3\dot{C}H_2 + CO \tag{2.27}$$

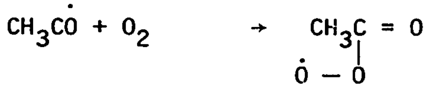
$$CH_3C\dot{O} \rightarrow \dot{C}H_3 + CO \tag{2.28}$$

$$HC\dot{O} \rightarrow \dot{H} + CO \tag{2.29}$$

These radicals can also react with oxygen.



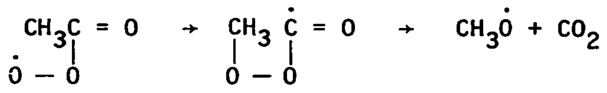
$$CH_3CH_2\dot{C}O + O_2 \rightarrow CH_3CH_2C(=O)-O-\dot{O} \qquad (2.30)$$



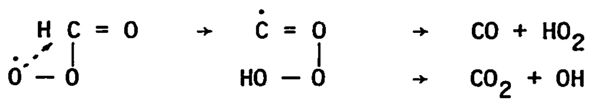
$$CH_3\dot{C}O + O_2 \rightarrow CH_3C(=O)-O-\dot{O} \qquad (2.31)$$

$$H\dot{C}O + O_2 \rightarrow HC(=O)-O-\dot{O} \qquad (2.32)$$

However, these reactions have low steric factors compared to the decomposition reactions and mostly the $H\dot{C}O$ radical and to some extent the $CH_3\dot{C}O$ radical are likely to enter into reaction with oxygen. The acetyl and formyl peroxy radicals can decompose with initial isomerization.



$$CH_3C(=O)-O-\dot{O} \rightarrow CH_3-O-O-\dot{C}=O \rightarrow CH_3\dot{O} + CO_2 \qquad (2.33)$$



$$HC(=O)-O-\dot{O} \rightarrow \dot{C}(=O)-O-OH \rightarrow CO + HO_2 \qquad (2.34)$$

$$\rightarrow CO_2 + OH \qquad (2.35)$$

An alternative for these peroxy radicals would be to react with a hydrocarbon molecule forming acyl hydroperoxide. However, at higher temperatures, decomposition will prevail.

The hydroxy radical formed in the system reacts with a paraffin molecule.

$$RH + \dot{O}H \rightarrow \dot{R} + H_2O \qquad (2.36)$$

The fate and role of the hydroperoxy radical ($H\dot{O}_2$) is still a matter of controversy. Some investigators suggested that it can attack a paraffin molecule especially in a fuel rich system as follows:

$$RH + H\dot{O}_2 \rightarrow \dot{R} + H_2O_2 \qquad (2.37)$$

Others, including Knox do not believe the above is an important reaction. Knox(9,10) quite recently made a bold attempt to explain the hydrocarbon oxidation reaction by considering the activities of the different free radicals. He suggested that the $H\dot{O}_2$ radical is quite inert, but is sufficiently reactive to combine with the olefins. A chain reaction is then started leading to the formation of oxygenated products and the transformation of the $H\dot{O}_2$ radical to $\dot{O}H$ radical. This transformation is basic to the theory of Knox, since his experimental results suggest that 80 per cent of the initial products of alkane oxidation are conjugate olefins by reactions of the type (2.3) and (2.4) which invariably produces the hydroperoxy radicals. The overall route for the transformation of the $H\dot{O}_2$ radical is

$$AB \xrightarrow{H\dot{O}_2} ABOOH \xrightarrow{O_2} \dot{O}OABOOH \xrightarrow{H\dot{O}_2} HOOABOOH \rightarrow AO + BO + 2\dot{O}H \qquad (2.38)$$

where AB denotes a conjugate olefin. Knox has very simply accounted for the negative temperature coefficient by suggesting that at that temperature region, the above mechanism fails and HO_2 becomes the major propagating species. At still higher temperatures, the reaction picks up again because of the thermal pyrolysis of hydrogen peroxide to $\dot{O}H$ radicals, which once again take up the propagating role.

Recently, Hughes and Simmons(11) studied the reaction of n-pentane with oxygen in the range 257 to 280°C at initial pressures which cover both the slow oxidation and cool flame regions. They obtained

60% of the initial products as acetone and found that cool flame formation is accompanied by relatively large amounts of olefins. Holtzmeier and Albright(12) studied propane oxidation by introducing propylene in a reacting stream. As the concentration of propylene increased to 10%, the induction period decreased by 20% and the overall kinetics of the reaction increased. The induction period decreased at higher concentrations of propylene. No significant role of propylene, on the whole, was observed. Similar conclusions were drawn earlier by Satterfield and Wilson(4). Lucquin and coworkers(13) suggested that at temperatures 270° to 350°C, olefins are formed by a heterogeneous isomerization process which becomes mainly homogeneous in the negative coefficient zone.

2.3 EFFECT OF REACTION VARIABLES

The operating conditions for the partial oxidation reactions vary to some extent with the paraffin being used, the higher paraffins being more oxidizable than the lower ones. The range of operating conditions normally encountered in the laboratory or pilot plant are as follows:

Temperature	300 to 500°C
Pressure	0.2 to 15 atm
Paraffin to Oxygen Ratio	1:1 to 15:1
Residence Time in Reactor	0.1 to 10.0 sec and up to several hours.

In general, lower pressures require higher temperatures and/or residence times. Higher pressures favour the formation of oxygenated compounds, and higher temperature promotes olefin formation, while higher oxygen to hydrocarbon ratio oxidizes greater amounts of initial hydrocarbons and promote greater formation of carbon oxides and water. Runs at pressures below atmospheric and higher residence times are likely limited to the laboratory.

Duthie(14), Dalla Lana(15), Musgrove(16) and Anderson(1) carried out experiments to determine the effects of temperature, pressure, residence time, and inlet gas composition on the vapour phase oxidation of n-butane at the University of Alberta between the years 1950 and 1966. Anderson designed and built a tubular reactor 0.625 inch diameter and 9 foot length of 316L stainless steel, with five sample points along the length of the reactor. Gas and wall temperatures were measured at different points along the reactor by thermocouples. The control of all reaction variables, temperatures, pressure and reactant flow rates, was accomplished by the use of either pneumatic or electronic controllers. Experiments were conducted at three temperature levels of 685°F, 705°F and 725°F, and indicated the dependence of the induction period on the inlet temperature. Runs were also made at four different inlet oxygen concentrations to study its effect on the overall reaction. The reactions gave a 60% conversion of the n-butane reacted to olefins for most of the runs. Only 10% of the n-butane that reacted went to carbon oxides. Of the remaining 30%, 10% went to lower molecular weight paraffins and 20% to oxygenated products. The oxygenated products consisted of aldehydes, ketones and alcohols. The gas temperature for any run remained fairly constant during the induction period and then increased rapidly to a peak temperature approximately 400°F above the inlet temperature. After the period of rapid reaction, the gas temperature decreased gradually because of heat transfer from the gas to the reactor wall. The period of rapid reaction during which the temperature shot up by about 400°F was

0.1 to 0.2 sec.

Quon, Dalla Lana and Govier(17) obtained an increased yield of oxygenated products by an increase in the reactor pressure. An optimum pressure of 125 psia was obtained for the reactor at a residence time of 1.2 to 1.8 sec. operating at a temperature of 725°F and inlet n-butane to oxygen ratio of 1:1 in the presence of 90% nitrogen.

The effects of surfaces on the partial oxidation reaction is known, but its role is not clearly understood. Surface effects of importance include surface to volume ratio of the reactor, the nature of the surface, and the treatment or coating of the surface. The reactor wall in many cases can play an important role in the initiation and termination steps in the free radical reaction(12).

Knox(18) has recently postulated that considerable part, if not the whole of the minor products are formed in heterogeneous processes, which by consequence play a very important role in the range from 230 to 350°C and subatmospheric pressure. He arrives at this by way of explaining why the ratio of major to minor products is little affected by composition, total pressure, temperature or surface, while the distribution of minor products is highly sensitive to these parameters. The minor products by the definition of Knox are the oxygenated products and the major products are the olefins.

Euker and Leinroth(19) oxidized n-butane in a flow reactor at 352-425°C and at pressures of 0.25 - 6.5 atm. Unlike Knox, they did not observe the major role being played by the surface. At 425°C and lower pressures, surface effects appeared to be important for some of the cracking products.

Albright(20) observed that the surface effects tend to decrease as the pressure increases or as the diameter of the tubular reactors increase. The ratio of surface of the reactor wall to the mass of the reaction mixture appears to be a very important factor relative to surface effects. For pressures of at least 6 atmospheres and for reactors with diameters of 5 to 6 inches or greater, surface effects may be inconsequential and gas phase reactions would be controlling. Surface effects in industrial reactors are probably of minimal importance.

2.4 METHODS OF CONTROLLING THE REACTION

The hydrocarbon oxidation is almost nonselective. The conversion of the hydrocarbon is generally low and the reaction leads to the formation of a large number of oxygenated compounds, lower paraffins, olefins, carbon oxides and water. A large amount of gas has to be recycled and the separation of the complex mixture of gases is difficult and expensive. Optimizing the yield of the reactor is vital to the economy of the entire process. Efforts in this area were directed to initiation at lower temperatures, use of homogeneous catalytic additives, removal of the intermediates as they are formed and at controlling the temperature of the reactor.

The hydrocarbon oxidation can be initiated at temperatures down to room temperature by supply of energy from outside, e.g., by photodissociation of certain chemicals which can supply free radicals, or by penetrating radiation such as r-rays which can generate free radicals in the system(8). However, these lead to very small conversions and are useful in mechanism studies alone.

The effect of a large number of homogeneous catalytic additives such as NO_2, Cl_2, Br_2, HCl, N_2, etc. has been studied by several investigators$^{(21)}$. The overall effect of these additives has been to shorten or eliminate the induction period by facilitating the initiation of the active centres, or to decrease the temperature of ignition and reaction. This sometimes leads to an improvement in selectivity.

Rust et al$^{(22)}$ studied the effect of addition of hydrogen bromide on the oxidation of different hydrocarbons. It was observed that in the presence of a tertiary bond in the hydrocarbon molecule the main oxidation product is an organic peroxide; if there are secondary bonds, the main oxidation product is ketone, and a hydrocarbon with a primary C-H bond leads mainly to organic acids. Thus, the addition of HBr leads to a significant change in selectivity and the oxidation presumably follows a different course. The oxidation temperature decreased by 100-120°C. For example, the oxidation of $\underline{i}$-C_4H_{10} occurs in absence of HBr at 265°C while with 20% HBr it occurs at 155-165°C. Further investigations are needed to confirm these findings.

Schubert and Pease$^{(23)}$ studied the oxidation of methane, propane, butane and iso-butane in mixtures with oxygen in the presence of about 3 per cent ozone under static and flow conditions at temperatures of 25-50°C and 170-270°C. In the case of propane and butane, it was noticed that the addition of ozone eliminated the induction period completely. A mechanism with initiating reactions of a hydrocarbon molecule with ozone forming an alkoxy radical and a HO_2 radical was suggested. Kleimenov et al$^{(24)}$ in a study of ozone oxidation of methane indicated that the reaction proceeds by ozone decomposition to give oxygen atoms which subsequently react with the hydrocarbon molecule. Dardrin and Albright$^{(25)}$ suggested the formation of a high energy propyl radical and an $\dot{O}H$ radical by reaction of propane with ozone.

$$O_3 + C_3H_8 \rightarrow O_2 + \dot{O}H + \dot{C}_3H_7^* \text{ (high energy propyl radical)} \quad (2.39)$$

Slavinskya et al(26) obtained higher conversion of n-butane and better selectivity for aldehydes in presence of ozone in the reaction mixture. In all cases, the induction period and the ignition temperature generally decreased.

Mitchel and Locke(27) allow a small amount of paraffin and air to react. This mixture which contains free radicals at a high concentration is injected as a side stream into the reactor. The side stream initiates reaction in the mainstream and an increase in selectivity has been observed. Jones and Fenske(28,29) obtained high yields of oxygenated products in a tubular reactor by controlling the reactor temperature by the introduction of inert solid particles as heat sink in the system.

Albright(30) quoted an industrial patent for an isothermal reactor. In one example, the hydrocarbon stream was preheated to 475°C and the oxygen stream was not heated. The temperature in the reactor was 500°C. In another example, both hydrocarbon and oxygen feeds were heated to 320°C and the reactor operated at 525°C. The presence of inerts such as NO_2, CO and CO_2 was claimed to be beneficial in controlling the rate of the reaction.

Oberdorfer and Winch(31) studied the oxidation of methane in a motored engine at a compression ratio of 40:1. The motored engine offers a means of effective control of the reaction because of its cyclic operation where high temperatures and pressures occur for very short periods of time and the reaction can be initiated and quenched easily by the proper selection of the operating variables. Methanol, formaldehyde and formic acid were the chief chemical products formed under nearly all conditions of operation. Carbon monoxide and hydrogen were formed concurrently in an amount under optimum conditions nearly equal to the total C_1 chemical products. Of the approximately 6% methane converted, approximately 40% formed C_1 oxygenated products, 33% formed CO and essentially no CO_2 was formed. Of the oxygen originally charged, approximately 44% was consumed in the reaction. Methane was obtained from a natural gas stock and 8% concentration of oxygen in 75% methane was found to be the optimum. The addition of 0.5% NO_2 in the gas nearly doubled the production of the chemicals, but shifted the optimum concentration of oxygen to 5-6%.

Gudkov(32) used a cold hot tube reactor for the oxidation of methane and propane. This is an annular reactor where the surface of the outer tube is hot (600 to 700°C) and that of the inner tube is cold. Gas passes through the annulus and water is circulated through the inner tube with a water film flowing past the outer surface of this tube. As a result of the great temperature gradient and convective flow, intensified diffusion exchange takes place in the annular space between the layers of gas at the hot and cold walls. Formaldehyde and other intermediates get dissolved in the water film and removed from the reactor with the water stream. Accordingly, in contrast to the method used in the partial oxidation in an ordinary tube in which the molecules of the intermediates formed must remain in a zone with reaction temperature for the entire length of time that is required for complete reaction, in the cold hot tube reactor they are removed from the reaction zone as they are formed. This should lead to an increase in the yield of oxygenated compounds and a decrease in the relative amount of by-products of the reaction. Gudkov obtained an increase of formaldehyde concentration

5 to 6 times for methane and 2 to 3 times for propane in a cold hot tube as against in an ordinary tubular reactor under comparable conditions.

2.5 TRANSPORTED BED REACTORS

Transported bed reactors have been used in industries for a long time, but little published information is available on their operations. In a transported bed reactor (henceforth referred to as TBR), a catalyst, an inert or a reacting solid is carried as a powder by gas through a long, narrow pipe line at velocities of 20 to 100 ft/sec. Generally, the solid is dilute in phase (less than 1% by volume) and can range in size from 40 to 1000 microns in diameters. Under these conditions, there is little backmixing of either gas or solids and the terminal velocity of solids through the gas is low compared with the absolute velocity of the gas; therefore, the contact time of the reactor can be accurately fixed. Also, the gas is fully turbulent and the solids can be considered to be uniformly dispersed through the cross-section of the pipe. Lower gas velocities complicate the residence time distribution and the uniform dispersion of the solids, but provide greater contact time between the solids and the gases for reaction and heat transfer. As the reaction proceeds with evolution of heat, the solid particles take up the heat of reaction and can maintain an essentially isothermal condition. With proper selection of the variables, it is possible to have the reactor temperature follow a certain chosen optimum path.

An exploratory study of TBR was made by Jepson and coworkers (33) for the thermal cracking of sodium bicarbonate. Dalla Lana(34) and Themelis and Gauvin(35) used this type of reactor for the direct reduction of iron oxide powder with hydrogen. Paetkau(36) used a TBR for the partial oxidation of o-xylene. The solid particles were fed to a horizontal section of pipe by a rotary solids feeder and then conveyed upwards by the reacting gases. Solid particles of average diameter 50 μ, density 131 lb/ft^3 were used at solids to gas loading ratios of 8 to 23 at a reaction temperature of 750°F. Othmer(37) has described a number of applications for TBR in industries.

Jones et al(28,38) used a reactor which they describe as a "raining" solids reactor where noncatalytic solid particles rain down against a countercurrent stream of gases. The solid particles are conveyed to the top of the reactor by dry steam. The reactor section is a 26 inch length of 1.5 in. diameter schedule 80 steel pipe and the operating conditions are 570°F to 1200°F at pressures ranging from atmospheric to 60 psig. A large number of solid particles such as fused alumina (125 μ), sand, glass beads (300 μ), mullite (300 μ), and zircon silicate (300 μ) were used at solids to gas loading ratios of 5 to 10. The oxygen was introduced at multiple points which also helped check the rise in temperature. The unit is operated in such a way that the oxygen added at one point is all consumed before the next oxygen inlet is reached. A large number of hydrocarbon stocks were investigated. At a reaction temperature of 400° to 420°C and a pressure of 50 psig, n-butane gave oxygenated compounds as the major products. At atmospheric pressure and the same temperature, olefins predominate.

The initiation of the reaction was found to be a function of the total pressure of the system, the solids surface area present, the quantity of diluent nitrogen and the geometry of the reactor. For the oxidation of ethane at 50 psig, the oxidation temperature was 100°C higher when 80-100 mesh particles were used compared to 35 to 40 mesh particles. This difference was apparently due to the larger surface area present for the smaller particles. This effect was not observed for the higher, more reactive hydrocarbons.

2.6 PRODUCT ANALYSIS

The most powerful single tool for the analysis of the combustion products is vapour phase gas chromatography. Since 1960, research workers in the field of hydrocarbon oxidation have almost exclusively used the gas chromatograph to analyze the products of the reaction(39). A number of instruments such as mass spectrometer, infrared spectrometer and N.M.R. have also been used in conjunction with the gas chromatograph. The coupling of a mass spectrometer with the gas chromatograph is very useful, as it provides simultaneous measurement and identification of the host of products that are formed in the hydrocarbon oxidation(40). Norrish and Porter(41) have used a gas chromatograph which takes samples directly from the reactor and the products are analyzed simultaneously in multiple columns using the same detector. Varkey and Sandler(42) have studied the oxidation of 2-methyl butane during the induction period using a flame detector in the gas chromatograph. The flame detector is about a thousand times more sensitive than the thermal conductivity detector usually employed, and is eminently suitable for studying the reaction during the initiation period.

2.7 SPECIAL EXPERIMENTAL TECHNIQUES

The usual method of studying the reaction is to determine quantitatively the product distribution as the reaction proceeds. The earlier studies almost exclusively measured the pressure change with the reaction. The change of temperature has also been used to study the reaction. Another interesting and very useful method seems to be the use of isotopes, employed by Russian workers and in increasing use now in hydrocarbon oxidation studies(43). Since the labelled atoms may be traced in the product, some of the finer details of the reaction can likely be elucidated.

2.8 SUMMARY

A vast amount of work has been reported in literature on the mechanism of the reaction of hydrocarbons with oxygen and the effects of different variables such as temperature, pressure and surface on the course of the reaction. Two major contenders emerge from the mechanism study in the last decade: the aldehydic mechanism of Semenov and Shtern and the olefinic mechanism of Knox. The suggestion of Knox that all the oxygenated products in the reaction are derived from heterogeneous reactions on the surface also merits serious consideration and has received considerable attention in recent literature.

The amount of work on the improvement of selectivity of the reaction products is rather limited. The pioneering works of Oberdorfer and Winch in a motored engine reactor, of Gudkov in a cold hot tube reactor and of Jones and coworkers in a raining solids reactor are very worthwhile efforts in this direction. Further engineering research is warranted to obtain successful tools in controlling the hydrocarbon oxidation reaction and to improve the selectivity to useful products.

CHAPTER III

SCOPE OF THIS WORK

The present work is a continuation of the overall study of the gas phase oxidation of hydrocarbons. A tubular reactor used earlier in this laboratory was modified to operate both as a homogeneous reactor and as a transported bed reactor. Solids feed and separation systems were designed and built. The solids were introduced into the system by a rotary solids feeder and were separated at the exit by a cyclone followed by a filter.

A mathematical model was formulated to represent the transported bed reactor system with temperature distribution in the solid particles. Numerical method for solving the system was developed and the solution obtained in order to evaluate the effects of particle material properties, the particle diameters and the gas to solid loading ratios on the heat removal efficiency of the system.

Runs were made in the homogeneous reactor to study the effect of inlet temperature and inlet n-butane to oxygen ratios on the overall oxidation process and on the product selectivity. The product selectivity data were used to suggest possible mechanisms for the reaction.

A number of runs were made to study the effect of adding solids in a transported bed reactor. The selectivity and overall oxidation of n-butane and oxygen, and the effect on the temperature profile in the reactor were compared with those for the homogeneous runs.

Parameters were estimated for the two kinetic models using the overall conversion and temperature profile data for homogeneous runs. The same models were used to predict the overall conversions and temperature profiles for the transported bed reactor.

CHAPTER IV

EXPERIMENTAL DETAILS

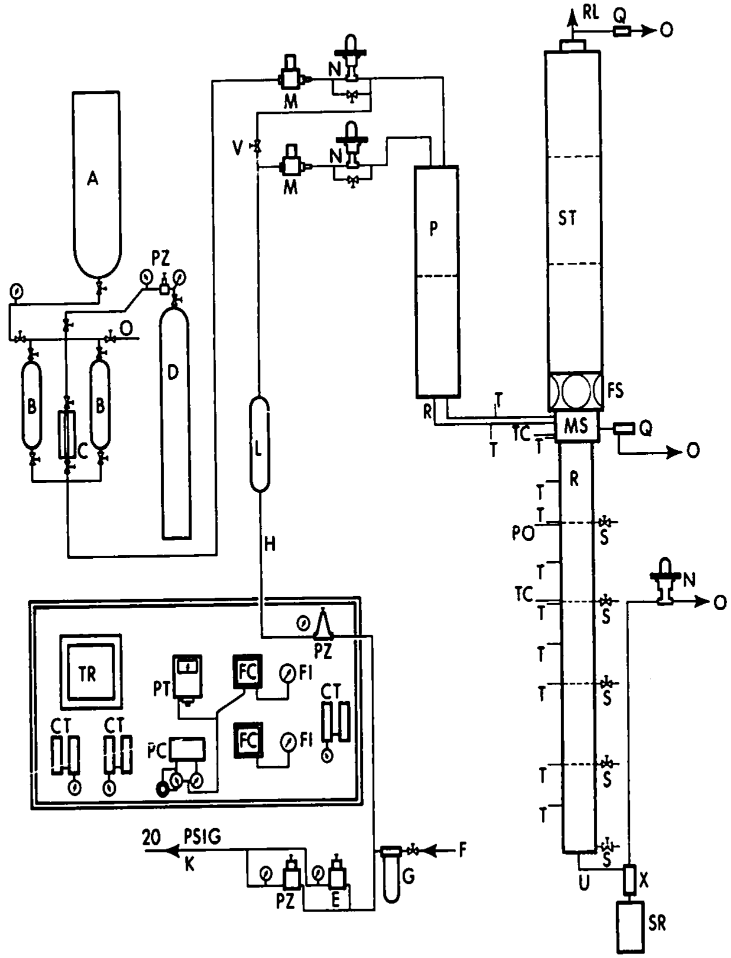
4.1 EQUIPMENT

A schematic diagram of the equipment and the associated instrumentation to control the feed rates, the reactor pressure and temperature, and the preheater temperatures is shown in Figure 4.1. The air and n-butane flow systems, the air and n-butane preheaters, and the temperature and flow control systems have been described in detail in an earlier investigation (1), and will not be discussed in great length here.

The reactor is a 9 foot length of 316L stainless steel tubing with inside and outside diameters of 0.625 inch and 1.25 inches, respectively. The gas preheaters are made of 3/8 inch 316 stainless steel. Both the reactor and the preheaters are heated by cylindrical Kanthal heaters and insulated by Johns Manville asbestos insulation. The _n_-butane is fed to the preheater as a liquid by nitrogen pressure. Air is taken directly from a compressed air line, after being passed through a pressure regulator and strainer to remove moisture or oil.

The solids preheater is a cylindrical tank 8 feet in length and 7.5 inches in diameter, fabricated from 1/8 inch mild steel sheet. The bottom section is made conical with an inside diameter of 2 inches to join with the solids feeder. The tank is surrounded by a tubular furnace made from Nikrothal 80 wire B and S gauge #11 (0.091 inch diameter) supported on Kanthal Y4-1286B bricks and insulated by fire-bricks.

The solids feeder, flange connected to the bottom of the solids heating tank, is a rotary valve. Each revolution of the rotor



A	BUTANE STORAGE
B	BUTANE FEED TANK
C	BUTANE LEVEL GAUGE
D	NITROGEN CYLINDER
CT	TEMPERATURE CONTROLLER
FC	FLOW CONTROLLER
F	AIR LINE
FI	FLOW INDICATOR
FS	SOLIDS FEEDER
G	WATER TRAP
H	PROCESS AIR
K	INSTRUMENT AIR
L	VOLUME TANK
M	INTEGRAL D/P CELL AND CHECK VALVE
MS	MIXING SECTION
N	CONTROL VALVE
O	EXIT & VENT LINES
P	PREHEATER
PC	PRESSURE CONTROLLER
PO	PRESSURE TAP
PT	PRESSURE TRANSMITTER
PZ	PRESSURE REGULATOR
Q	RELIEF VALVE
R	REACTOR
RL	LINE TO REACTOR
S	SAMPLE LINE
SR	SOLIDS RECEIVER
ST	SOLIDS PREHEATER
T	RECORDING THERMOCOUPLE
TC	CONTROL THERMOCOUPLE
TR	TEMPERATURE RECORDER
U	EXIT SECTION
V	BYPASS VALVE
X	CYCLONE AND FILTER

FIGURE 4.1 SCHEMATIC LAYOUT OF EQUIPMENT

transfers a fixed volume of solids from the tank to the solids discharge cone. The clearance between the rotor and the valve is very small (0.005 inch) in order that the valve may hold the solids when not in operation.

The valve rotor was machined from a 6 inch length of 4 inches diameter mild steel block. Grooves 0.045 inch x 0.045 inch in cross section were machined in the outer surface of the rotor, with a total of 136 slots.

The housing for the rotor was made from a 6 inch section of 4 inch diameter standard steel pipe. The solids entrance and exit ports are welded to the housing. An end plate is bolted to each end of the housing. The purpose of the end plates is to seal the unit and to provide bearings for the shaft. An o-ring seal is required to make the unit gas tight. The o-ring seal is made of high temperature graphite.

The valve shaft is connected to a variable speed drive. Heating wires were wrapped around the valve housing in order to prevent unequal expansion of the rotor and the housing.

Thermocouples are incorporated to measure the gas and wall temperatures in the reactor. Samples are taken out of the reactor at five points and are collected in small stainless steel bombs by actuating solenoid valves. The sample line is made of 1/8 inch stainless steel tubing and the sample stream passes through a filter made of sintered stainless steel before entering the solenoid valves.

The gas and solid streams in a TBR come out through a 1/2 inch diameter stainless steel tubing to a cyclone separator. The cyclone is made of mild steel and was designed with some modification of the specification given by Perry(44). The cyclone is followed by a filter made

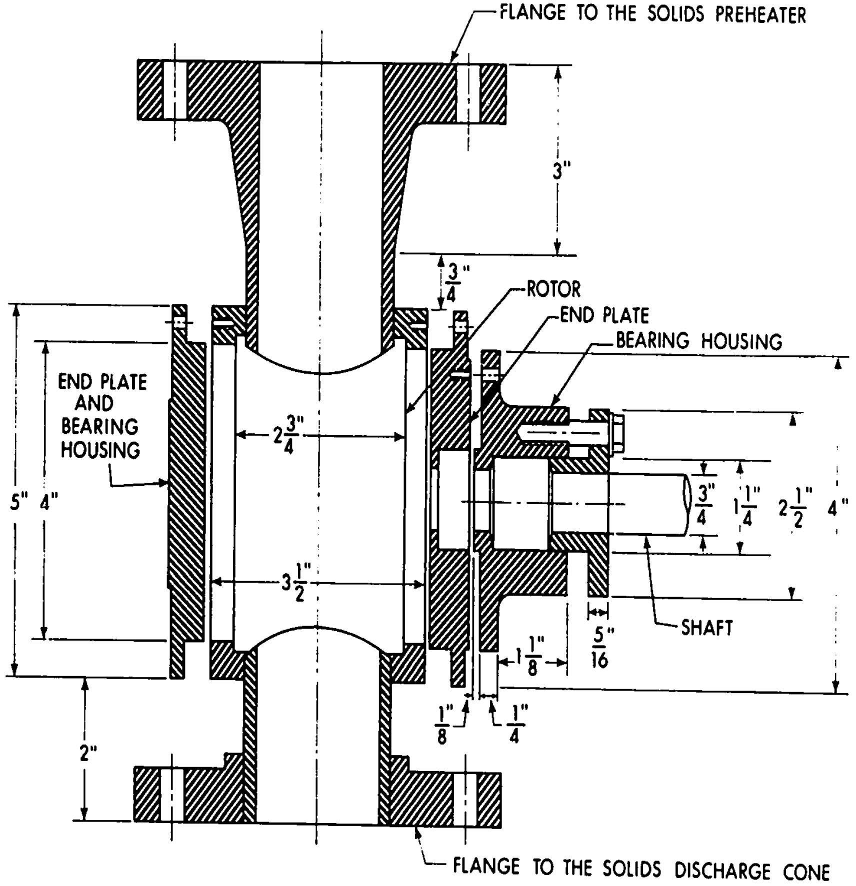


FIGURE 4.2 SOLIDS FEEDER

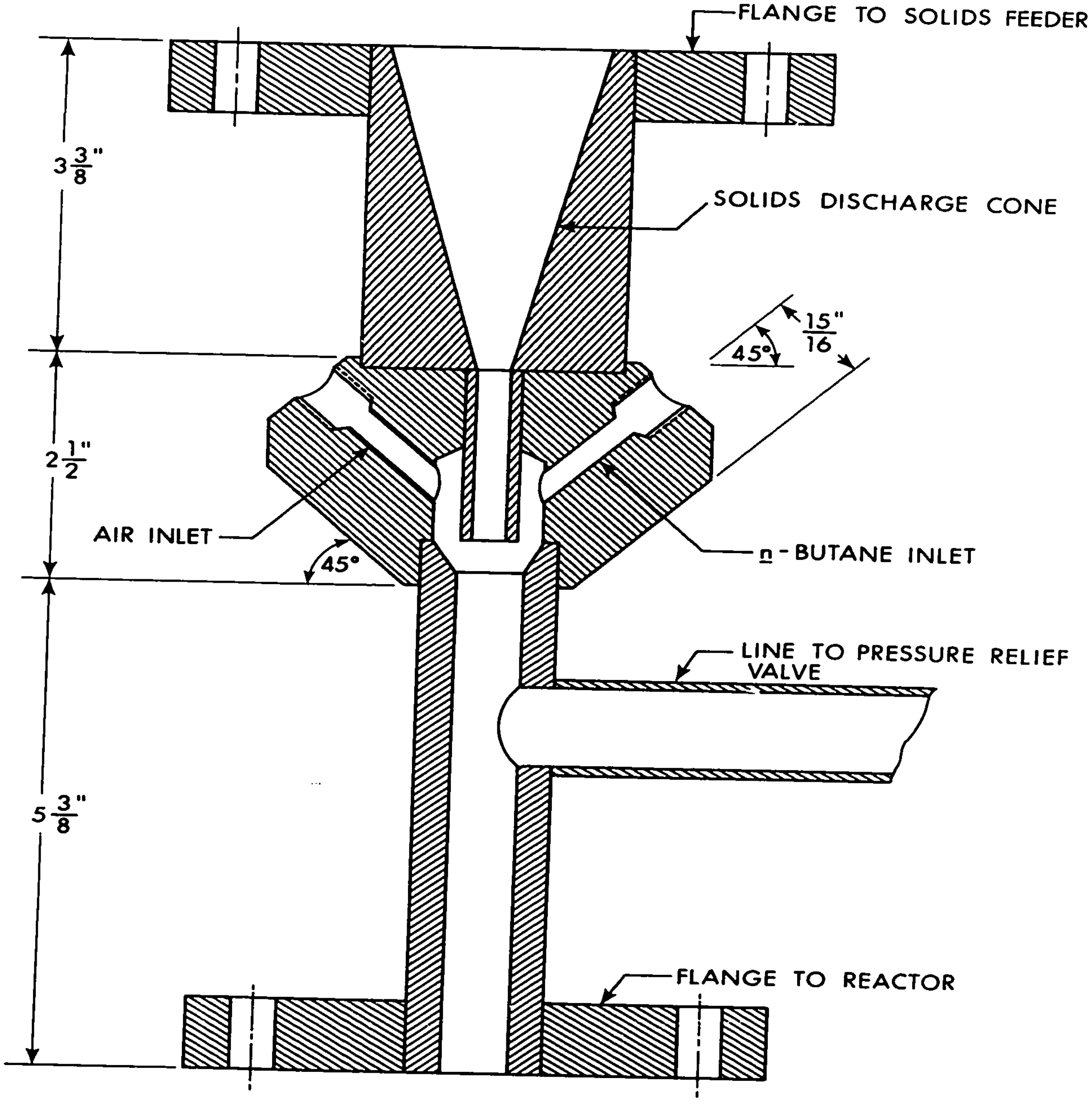


FIGURE 4.3 MIXING SECTION FOR GAS AND SOLIDS

of stainless steel screen, 400 mesh.

Diagrams of the solids feeder and the gas-solids mixing section are presented in Figures 4.2 and 4.3. Details of some features of the equipment are presented in Appendix A.

4.2 PRODUCT ANALYSIS

All product samples were analyzed using a Burrel Model KD gas chromatograph equipped with a thermal conductivity detector. A Sargent millivolt recorder model SR recorded the output of the chromatograph. Helium at air inlet pressure of 40 psig was used as the carrier gas for all the analyses. The helium passed through a drier cartridge of molecular sieve 5A to remove any moisture before entering the chromatographic unit. Helium flow rate was regulated for both the carrier and reference sides by Nupro metering valves and checked by timing soap bubbles in a gas burette. All product samples were injected into the column through the gas sampler built into the gas chromatograph. Since the sample contained condensable products, all lines before the column were heated by wrapping around heating tapes. The samples analyzed were under pressure and the injection was done by displacement. The sample size could be changed by changing sampler tubes of 1/8 inch stainless steel.

Two columns were used to effect the separation of the components in the mixture. Both columns were made from 3/16 inch soft copper tubing with Swagelok fittings on both ends and wound into spirals to fit into the temperature bath cabinet. The columns, their operating conditions, and the components separated are as follows:

Column 1: A 12 ft column packed with 80 to 100 mesh Porapak S made by Waters Associates.

Components separated: Paraffins, olefins, oxygenated hydrocarbons, carbon oxides and water.

Column Temperature: 50°C for the first 6 minutes followed by 10°C/min rise to 150°C, 10°C/min rise to 200°C after 30 minutes from the beginning.

Carrier Flow Rate: 42 cc/min

Reference Flow Rate: 40 cc/min

Detector Current: 200 ma

Gas Sampler: 12 inch long 1/8 inch tube, 0.75 cc volume

Column 2: A twelve ft column packed with high activity charcoal 40 to 60 mesh for the first six ft followed by an equal length of molecular sieve type 13X.

Components separated: Hydrogen, oxygen, nitrogen, methane and carbon monoxide.

Column Temperature: 40°C

Carrier Flow Rate: 35 cc/min

Reference Flow Rate: 30 cc/min

Detector Current: 250 ma

Gas Sampler: 5.5 inch long, 0.28 cc volume

The components were identified by their retention times. The retention time of a component is the time taken from sample injection to the maximum point in the peak. Retention times for the various components and examples of the chromatograms for each chromatographic column are reported in Appendix B.

4.3 OPERATING PROCEDURE

The preheater and reactor systems for a homogeneous run were first heated for a few hours with air only in the system. Before the introduction of n-butane in the system, the pressure of the reactor was raised to about 30 psig. This eliminated sudden build up of pressure when n-butane was introduced in the system and also allowed a rapid attainment of a steady pressure of 40 psig used in the study.

Before a TBR run was made, it was necessary to heat the solids for a long period of time. The solids were first heated for seventy-two hours and then the air streams turned on as in a homogeneous run. The heating was allowed to go on for another twenty-four hours in order to ensure steady solids temperature. A small leak of air at the top of the solids tank was found to aid in enhancing the solids heating rate.

Samples were taken in each run at steady state. Steady state was considered achieved when a steady temperature profile was obtained, as recorded by the multipoint temperature recorder. The samples were stored in an oven at 110°C to be analyzed in a gas chromatograph.

4.4 CALIBRATION OF EQUIPMENT

Calibration of the integral D/P cells for n-butane and air flow rates, and the pressure transmitter was carried out prior to the start of the experimental program. Calibration procedures and curves are presented in Appendix C. The calibrations were checked at random intervals during the progress of the experimental investigation.

4.5 EXPERIMENTAL DIFFICULTIES

A number of serious experimental problems were encountered during the progress of this investigation. This section describes some of them. The development work needed to solve those problems is also included.

The development of a satisfactory method of feeding the solids posed a major problem. The high temperature and pressure both act contrary to the satisfactory performance of any solids feeder.

Initially, an orifice feeder with solids heating in spiral tubes was investigated. The orifice feeding accomplished by applying differential pressure in the solids tank was found to be very uniform and highly reproducible, but the heating system was not satisfactory. The possibility of solids plugging always remains in a gas solids system, and no satisfactory solution could be possible once it occurs in spirally coiled tubes.

The method of heating was therefore changed to heating in batch in a tank. This, however, posed a problem for orifice feeding because of the difficulty in the design and operation of a valve which would operate satisfactorily.

The use of a screw feeder was explored, but was abandoned because of the nonuniformity of flow.

The rotary solids feeder finally adopted for the system has been on the whole very satisfactory. The solids flow is uniform and reproducible. Initially, there was jamming of the rotor. This was likely due to unequal expansion of the rotor and the housing, and was remedied by heating the housing. The solids feeder operates with a lot of vibration and a strong foundation is necessary.

In the earlier evaluation of the solids feeder, the solids backflowed and came out through the entrance lines. This happened once because of a leak in the upstream section of the air line and again because of a pressure build up in the reactor. Care has to be taken to avoid such incidents.

The solids separation system also gave some serious trouble. The initial cyclone was not adequate and there was appreciable carry over even from a filter used at that time. A small amount of solid particles passing for a short time can significantly erode the exit valve in the reactor. The clearance between the solids rotor and housing is small, but even then some solids can pass through when there is a sudden change in pressure and flow rates in the system. Some care has to be taken to avoid sudden change in these quantities when solids are in the system. The disturbance during the start-up was eliminated by raising the pressure of the reactor to 30 psig before the introduction of n-butane. The shut down also needs some manipulation and adjustments.

CHAPTER V

EXPERIMENTAL PROGRAM

5.1 REACTION VARIABLES

Preliminary evaluation of the homogeneous reactor suggested gas temperature profile as an index to the overall reaction and the product selectivity. The inlet temperature affected the length of the induction period without significantly affecting the further course of the reaction. Increase in oxygen concentration led to a higher overall conversion of *n*-butane, but a lower yield of the oxygenated compounds. Attempts were directed at improving the selectivity and also to obtain samples at different regions of oxidation so as to be able to evaluate the progress of the reaction.

Homogeneous runs were conducted at three temperature levels of 687°F, 702°F and 708°F, and at four different hydrocarbon to oxygen ratios of 14, 11, 8.7 and 7.7. In all the runs, oxygen was obtained from air which resulted in a definite percentage of nitrogen in the reaction stream.

Details of the experimental runs are given in Table 5.1. The experimental temperature profiles are presented in Table D.1 in the Appendix.

The runs in the transported bed reactor are described in Section 7.3.1.

5.2 RAW MATERIALS

The experimental runs were made with C.P. grade *n*-butane supplied by Matheson of Canada Ltd. Chromatographic analysis of several samples gave a purity of over 99.5 per cent. The rest were propylene

TABLE 5.1

Experimental Run Details

RUN NO.	INLET TEMP. °F	PRESSURE psia	*n*-BUTANE: OXYGEN	RESIDENCE TIME sec	INLET REYNOLDS NUMBER
60	685	53.6	14.0	1.41	6358
61	695	53.7	11.0	1.37	6088
62	695	53.7	8.7	1.25	6199
63	702	53.6	6.9	1.16	6154
64	692	53.6	7.75	1.42	5402
65	687	53.5	7.37	1.23	6072
66	708	53.4	7.79	1.21	6080
67	684	53.6	5.73	1.56	4446
68	684	53.7	8.01	1.43	5357

and i-butane.

The oxygen for the reaction came from air. Analysis of the air revealed no trace compound.

The solid particles used in the transported bed reactor were silicon carbon powders supplied by Norton Company of Canada. The physical properties of these powders are given in Appendix A.

5.3 CHROMATOGRAPHIC ANALYSIS

All product samples were analyzed in a Burrel Gas Chromatograph. The components of the samples were identified by their retention times. The retention times for each component were determined for each component individually and then checked by running several known mixtures of the components. The retention times for each component are given in Table B.1.

The peak area for each component was determined by multiplying the peak height by the width at half the height. This was converted to molar composition by using a relative response factor as described by Rosie and Grob(45) and Messener *et al*(46). As the response factors are valid at constant temperature, and temperature programming was used in the present work, correction factors were obtained and these are presented along with the retention times in Table B.1.

CHAPTER VI

HOMOGENEOUS REACTOR: RESULTS AND DISCUSSIONS

6.1 Introduction

The performance of the equipment and the associated gas chromatograph has been reviewed. The experimental temperature profiles and the overall conversions have been plotted and the effects of inlet temperatures and inlet n-butane to oxygen ratio discussed. The dependence of the formation of different products on the same variables is enunciated with the help of plots of selectivity versus residence times. The conclusions formed thereby are further augmented by considering the reaction at low residence times and low conversions. A qualitative description of a possible mechanism that may be taking place is presented.

Two simplified kinetic schemes are proposed to describe the temperature profiles and the overall conversions of n-butane and oxygen in the reactor. The parameters of the models are estimated by using a numerical method. The models are tested by using them to predict the temperature profiles and conversions for a number of runs in an earlier work in this laboratory.

6.2 Equipment

The performance of the equipment as a whole was satisfactory. There was a maximum error of ± 1 per cent of the weight rate of flow of n-butane and air, because of a ± .5 per cent deviation on the recorder chart. Sensitivity analyses show that this, however, can introduce an error of ± 10°F in the maximum temperature attained. The reactor pressure was maintained fairly constant and no significant effect was observed for the ± 1 per cent deviation that occurred in the different runs. The preheater temperature controller varied by ± 2°F. This introduces a fluctuation in the maximum temperature by ± 40°F. The reactor temperature controller was used mainly in preheating the reactor and was not normally effective otherwise. The observed ± 50°F variation in the maximum temperature did not apparently introduce significant variations in the product distribution.

6.3 Product Analysis

Quantitative analysis of the reaction products was made by the use of relative response factors as described by Messener and coworkers (46). In order to check the accuracy of the method, a test sample was prepared and analyzed on the gas chromatograph. Results of the test sample are presented in table 6.1. Use of relative response factor limited the error within about ± 5 per cent of the true value as compared to ± 10 per cent if the area per cent is assumed equal to the weight per cent. The relative response factor for water given by Rosie and Grob(45) as 0.21 was found to be in considerable error. A new and corrected value of 0.31 was obtained and used in the quantitative analysis. The response factors for methanol and ethanol were also slightly

TABLE 6.1

Test Sample with Compositions Calculated Using

Relative Response Factors

Compound	True wt %	True Mole %	Observed Area %	Calculated Mole %
Water	8.81	24.54	8.1	23.64
Methanol	7.66	12.0	8.33	12.35
Ethanol	9.48	10.32	9.63	10.35
Propionaldehyde	15.04	12.98	13.89	13.28
_n_-Propanol	14.24	11.88	15.70	12.74
Methyl ethyl ketone	19.74	13.73	20.86	14.06
Diethyl ketone	25.0	14.55	23.40	13.53

out and were corrected. The response factors are generally obtained at constant temperatures. Since temperature programming is used in the present analysis, correction factors were calculated for each component, because the peak areas generally increase at elevated temperatures.

The analysis of the actual reaction mixture is very complicated because of the number of components and of the wide range in proportions in which they are present. The areas of the peak were calculated by the height-width method. There are four major areas of indeterminate errors in the measurement of peak areas by this method: placement of the base line, measurement of height from base line, positioning of the measuring instrument at a predetermined height, and measurement of the width. Harris and Kratochvil(47) combined all four errors statistically for peaks of constant area but of varying height to width ratios and obtained a minimum in the relative error at ± 2 per cent at a peak height to width ratio of 3. The relative error increases quite sharply at all other ratios, especially at lower ratios.

The major components in the reacting mixture are air and _n_-butane. The peak height to width ratio for air peak is about 40 and both the air and _n_-butane peaks are attenuated by a large amount. Besides, most of the oxygenated compounds are present in small amounts and have low peak height to width ratios. These factors introduce uncertainties in the analysis of the reaction products and would be responsible for the relatively poor oxygen balances of 80 to 100 per cent. The carbon and hydrogen balances are mostly bound within 95 to 100 per cent.

Analysis of a gas sample which contained a very large amount of one component relative to the others gave excellent reproducibility. A standard natural gas sample supplied by Phillips Petroleum Company was obtained from another laboratory(48). Table 6.2 shows that the results obtained in the three laboratories are in good agreement.

TABLE 6.2

Analysis of a Standard Gas Sample

Component	Phillips	Energy Resources Conservation Board	Present Work
He, O_2, N_2	6.02	6.05	6.06
Carbon dioxide	1.32	1.32	1.26
Methane	71.50	71.59	71.50
Ethane	7.33	7.10	7.40
Propylene	0.02	-	0.03
Propane	5.95	5.92	6.03
Isobutane	3.00	3.01	2.98
_n_-Butane	2.90	3.02	2.85
iso-Pentane	0.98	0.99	0.95
_n_-Pentane	0.98	1.00	0.97

6.4 Experimental Results

6.4.1 Temperature Profiles

Temperatures of the reacting gas stream were measured by nine thermocouples along the length of the reactor. All temperatures are listed in table D.1 in the appendix.

For any experimental run, the gas temperature first decreases and then increases very sharply, followed by a gradual decrease again. The initial decrease takes place for the length of the induction period

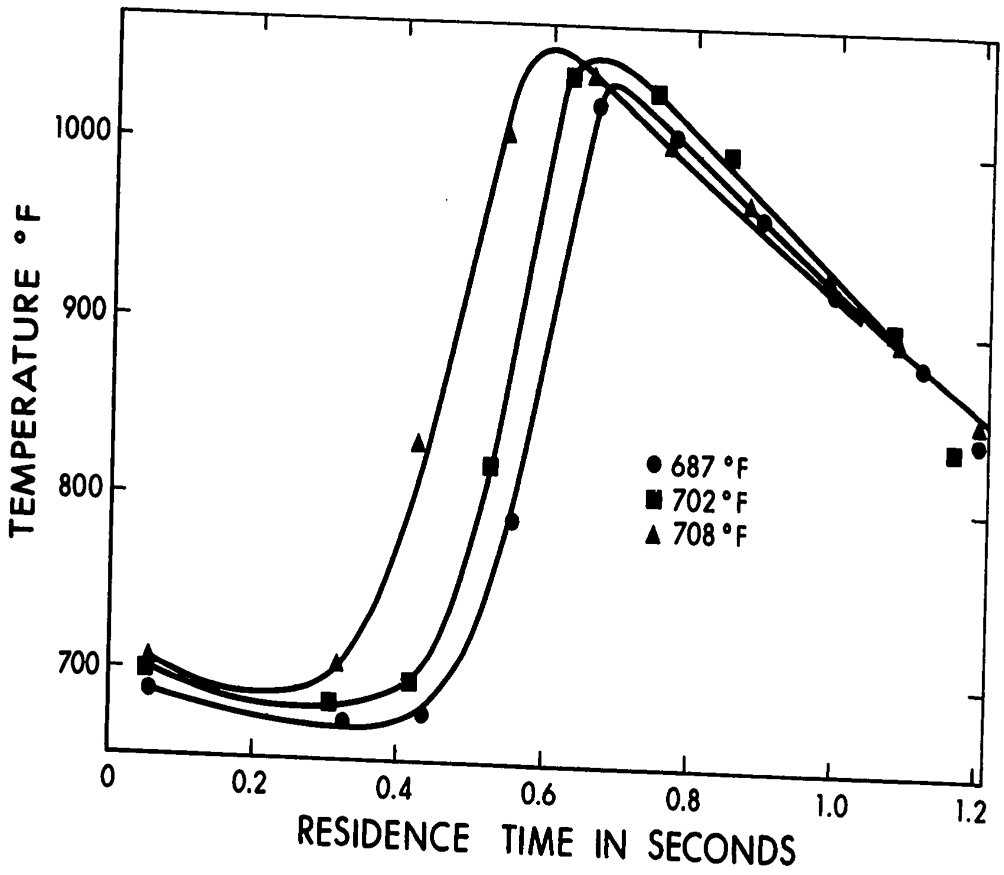


FIGURE 6.1 REACTOR TEMPERATURE PROFILES - EFFECT OF INLET TEMPERATURE

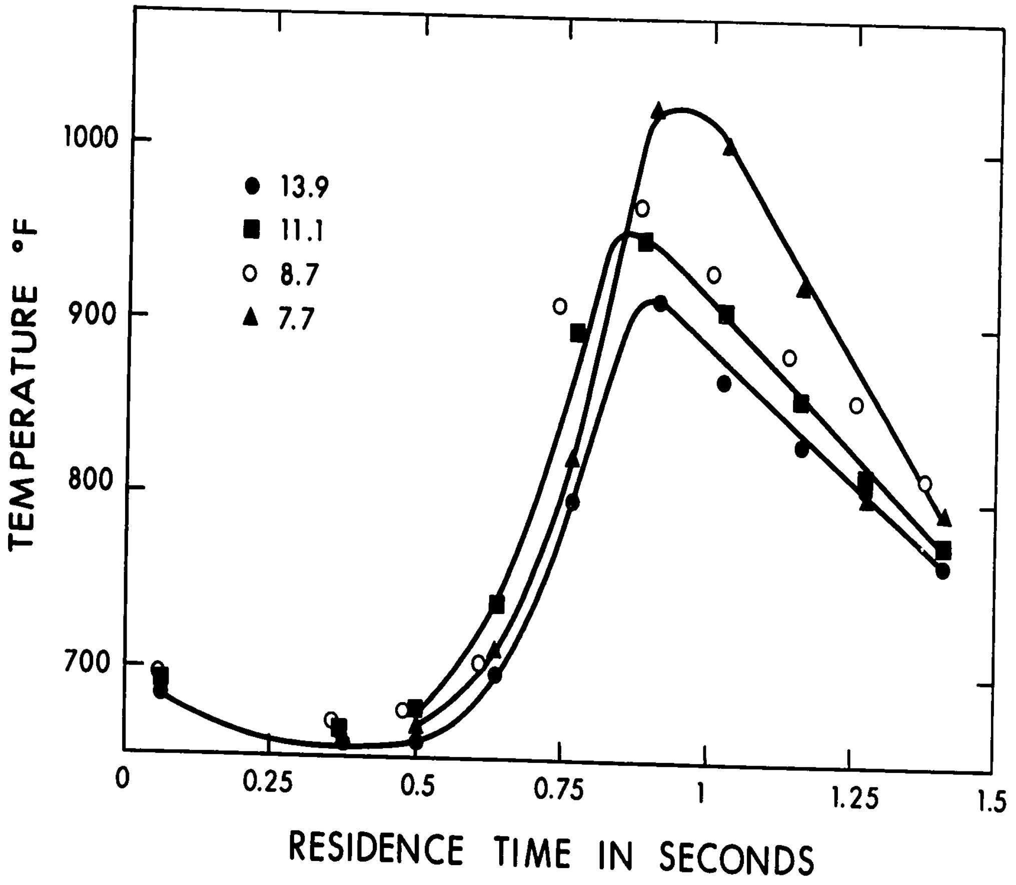


FIGURE 6.2 REACTOR TEMPERATURE PROFILE - EFFECT OF INLET MOLAR RATIO

by heat loss to the surroundings. The increase in temperature at the end of the induction period is due to a very rapid rise in the reaction rate which liberates a large amount of heat of reaction. The gas temperature rises by about 300-400°F in a period of 0.1 to 0.15 seconds. Any thermocouple located at this section showed a fluctuation of ± 50°F due to slight variations in flow rates and control temperatures.

After the period of rapid reaction, very little reaction takes place and the reacting stream slowly cools down by heat loss to the surroundings.

6.4.2 Products Formed in the Reaction

A large number of products are formed in the reaction. The study has been made with particular emphasis on the distribution of these products as affected by different reaction variables. For each run, five different samples were taken at different points along the length of the reactor. The major products of the partial oxidation of n-butane are paraffins, olefins, aldehydes, alcohols, water and carbon oxides. The paraffins are mostly methane and ethane, and the olefins are ethylene, propylene and n-butenes. The major alcohols are methanol and small amounts of ethanol, and formaldehyde and acetaldehyde are the principal aldehydes. Small amounts of propionaldehyde, acetone, methyl ethyl ketone and diethyl ketone are also formed. Propane, 2-methyl butane, n-pentane, propanol, butanol and butyraldehyde have also been isolated.

The method of reduction of the gas chromatographic data is outlined in Appendix E. The computer program and the results are also presented in Appendix E.

6.4.3 Effect of Reaction Variables

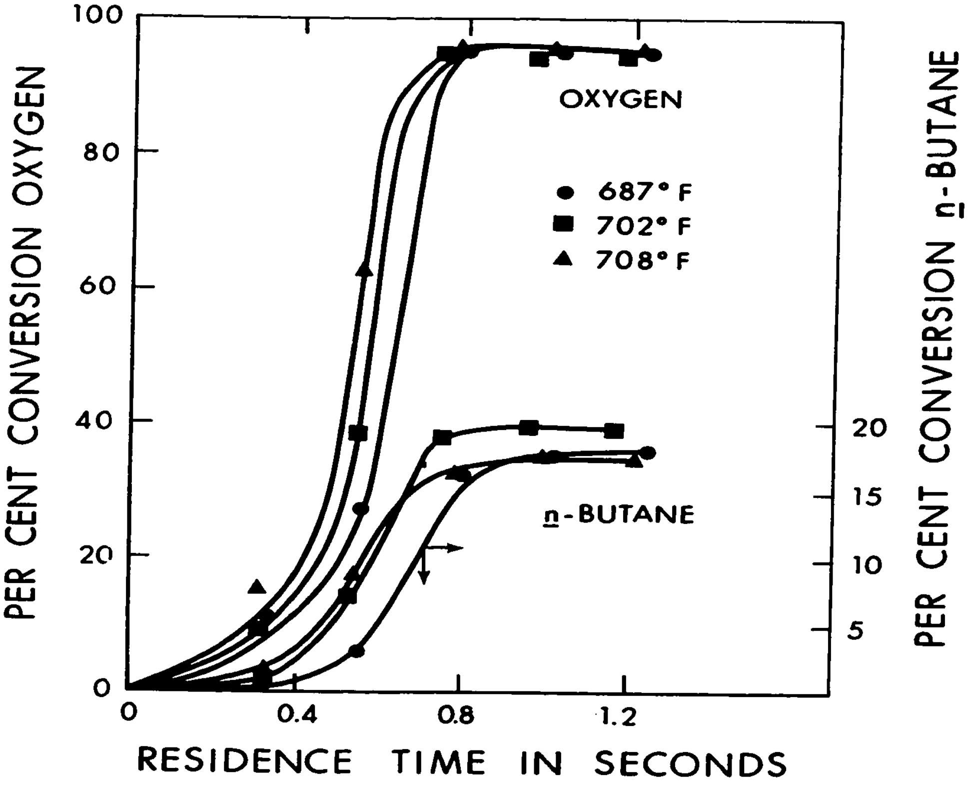


FIGURE 6.3 OVERALL CONVERSIONS - EFFECT OF INLET TEMPERATURE

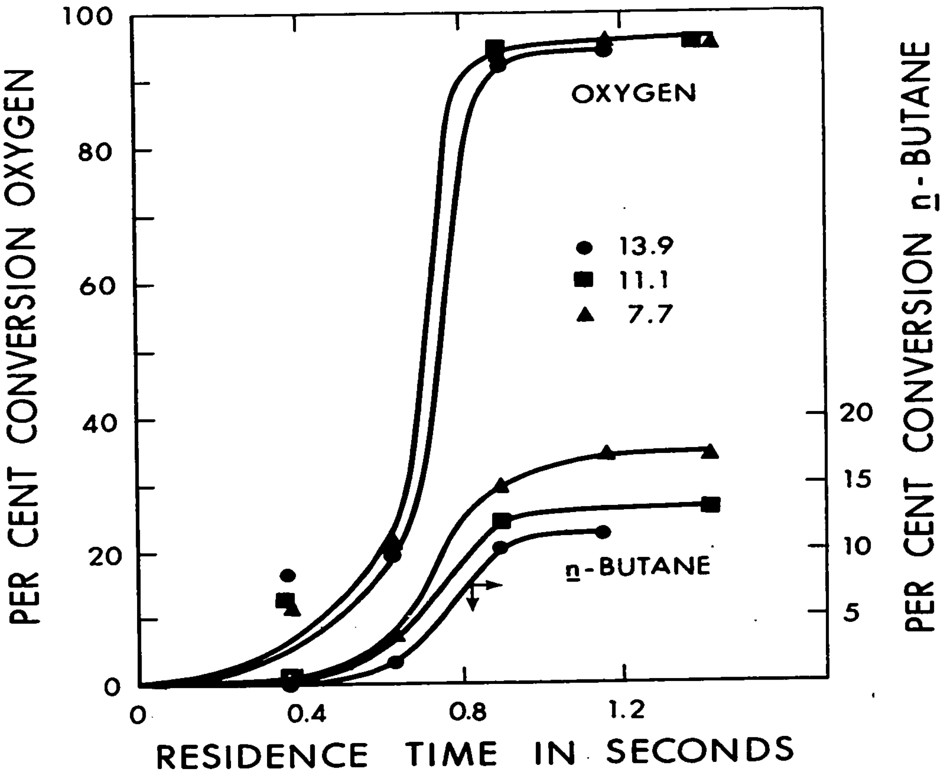


FIGURE 6.4 OVERALL CONVERSIONS - EFFECT OF INLET MOLAR RATIO

The reaction variables considered in this investigation are the starting temperatures and the starting n-butane to oxygen ratios. The starting temperatures investigated were 687°F, 702°F and 708°F, the run numbers being 65, 63 and 66, respectively. Runs 60, 61, 62, and 64 were carried out at inlet ratios of 14, 11, 8.7 and 7.7, respectively. The temperature profiles for these runs are plotted in Figures 6.1 and 6.2.

The starting temperature has a profound effect on the length of the induction period, but does not affect the rise in temperature once the induction period is over. The gases reach about the same maximum temperature at the end of the induction period.

On the other hand, as shown in Figure 6.2, the hydrocarbon to oxygen ratios do not have any significant effect on the length of the induction period, but lower ratios mean a greater temperature rise in the reactor. Some differences in the induction period for these runs are not due to the difference in the ratios, but rather because of some difference in the starting temperatures. Figure 6.3 shows that to reach a 10 per cent conversion of oxygen takes 0.36 seconds for the run at 687°F compared to 0.2 seconds for the run at 708°F. The period of rapid reaction lasts for about the same length of time for all the runs, about 0.15 to 0.20 seconds.

The overall conversion of oxygen is almost constant at around 95 per cent for all the runs. The conversion of n-butane depends upon the hydrocarbon to oxygen ratios, as shown in Figure 6.4. The conversion is lower for higher ratios. At a hydrocarbon to oxygen ratio of 14, the conversion of n-butane is approximately 13 per cent, while it is around 20 per cent at a ratio of 7.7. The higher conversion of n-butane is due

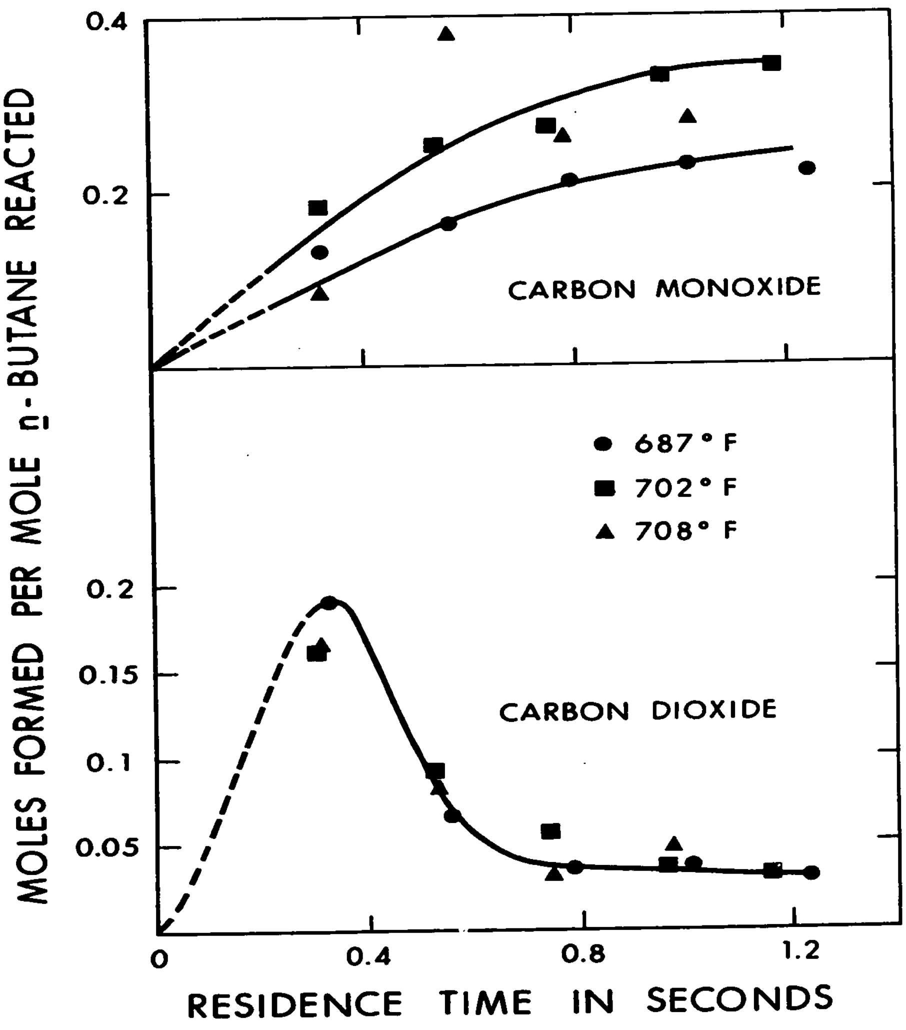


FIGURE 6.5 SELECTIVITY OF CARBON MONOXIDE AND CARBON DIOXIDE - EFFECT OF INLET TEMPERATURE

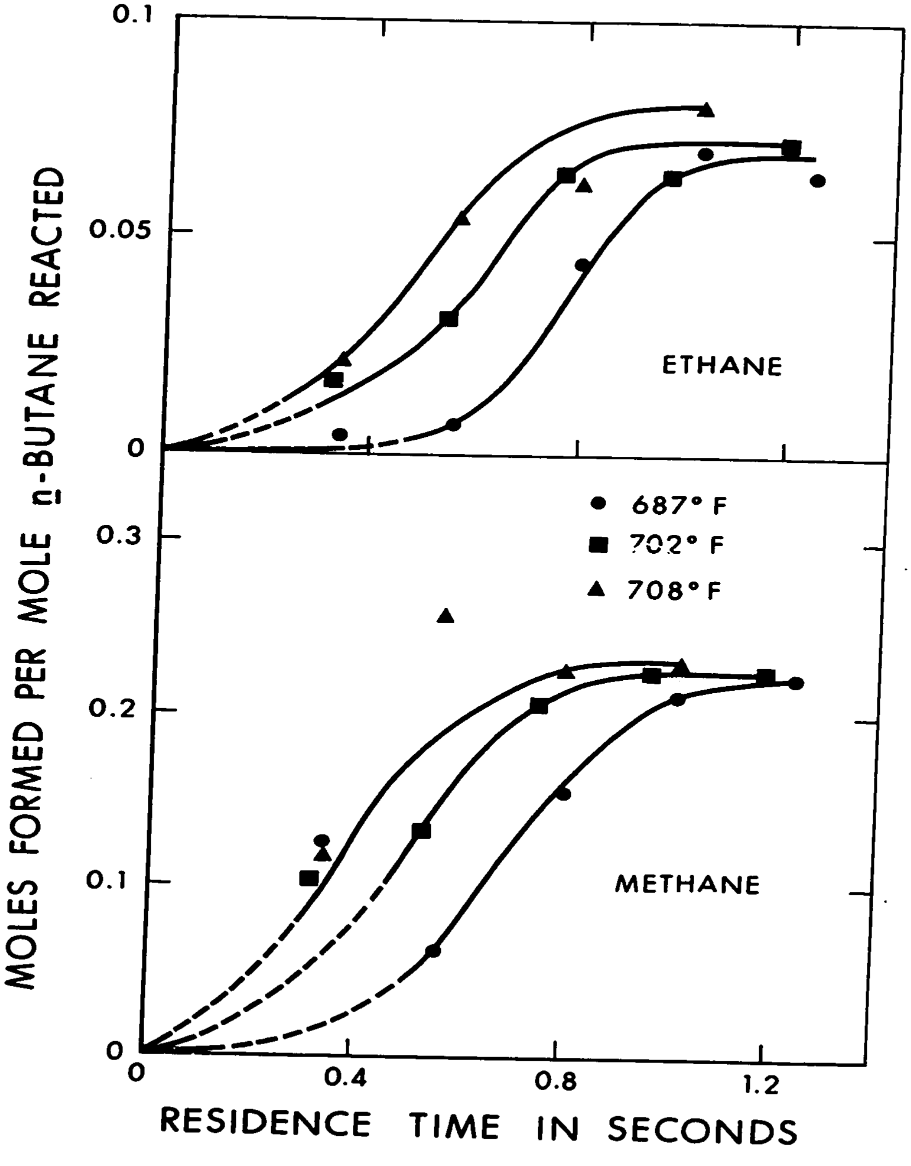


FIGURE 6.6 SELECTIVITY OF METHANE AND ETHANE-EFFECT OF INLET TEMPERATURE

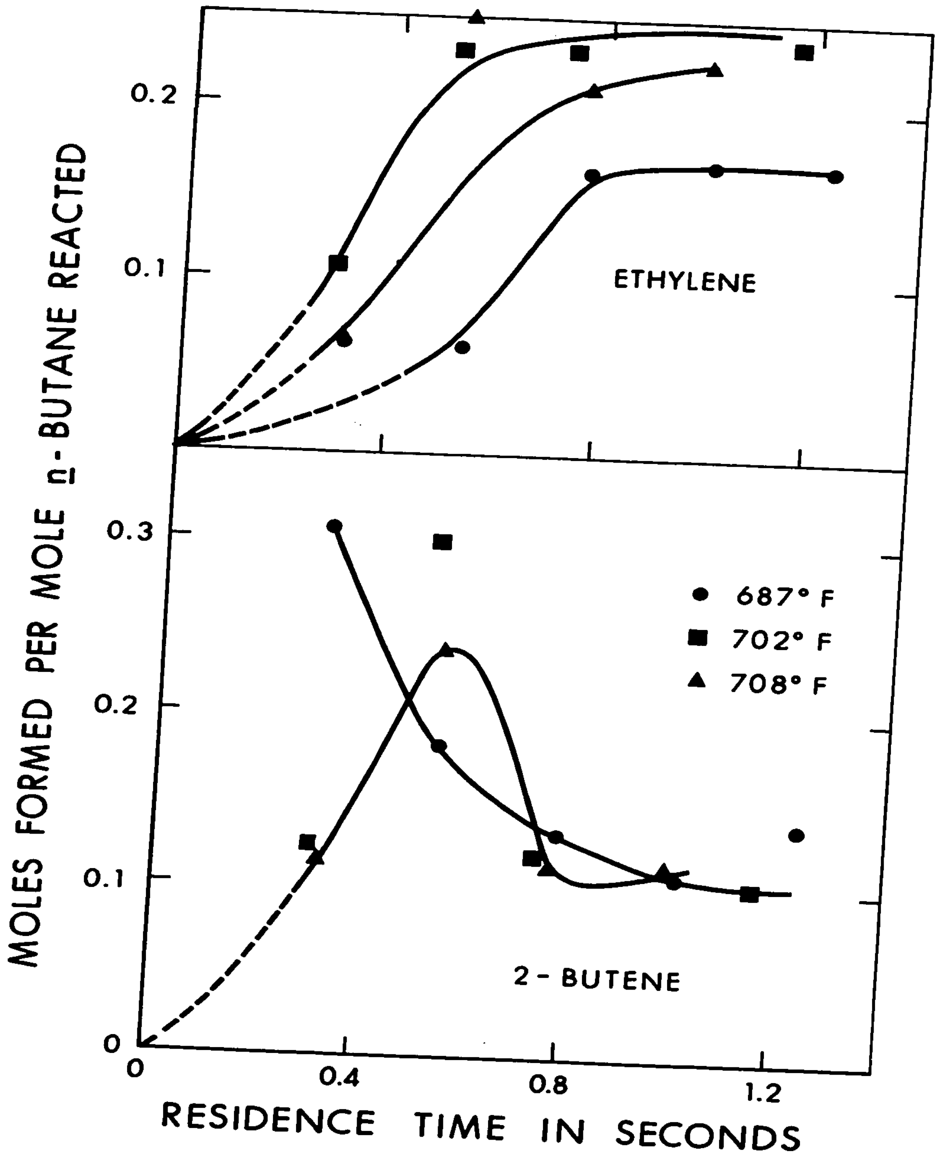


FIGURE 6.7 SELECTIVITY OF ETHYLENE AND 2 - BUTENE -EFFECT OF INLET TEMPERATURE

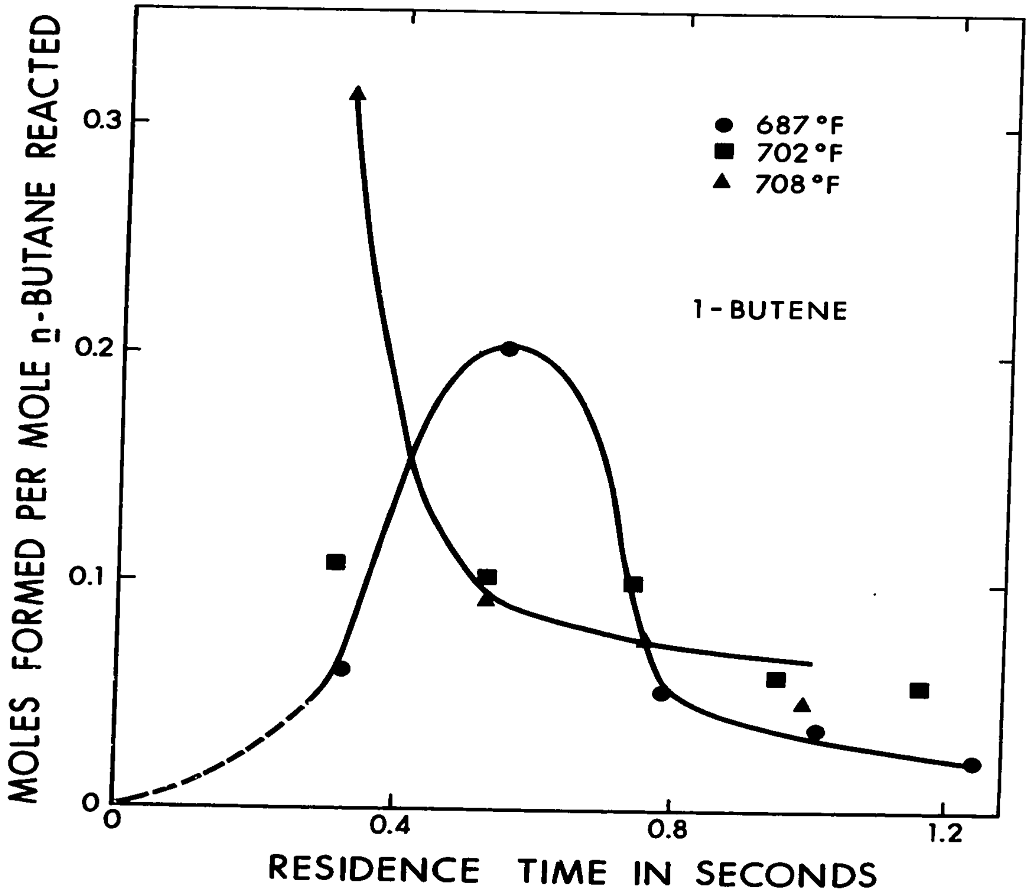


FIGURE 6.8 SELECTIVITY OF 1 - BUTENE - EFFECT OF INLET TEMPERATURE

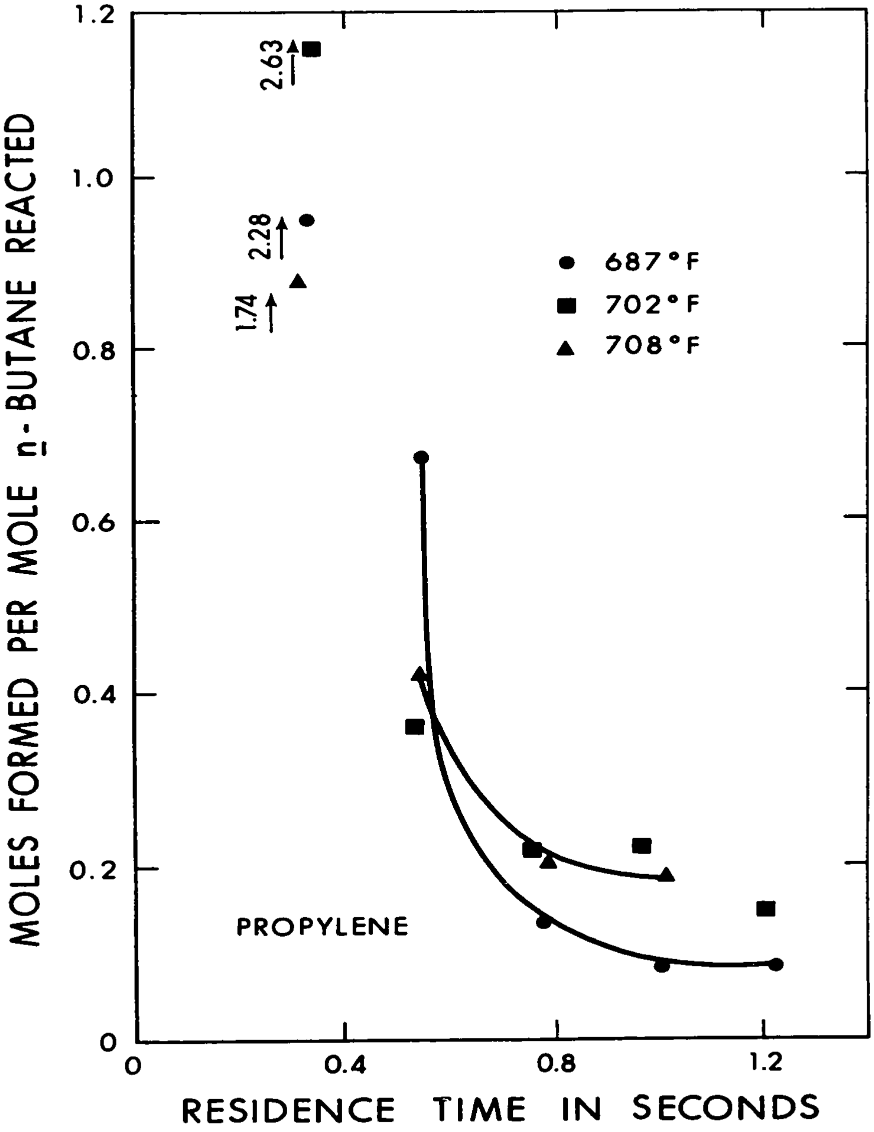


FIGURE 6.9 SELECTIVITY OF PROPYLENE - EFFECT OF INLET TEMPERATURE

to the availability of more oxygen in the system, but partly may be due to some cracking reactions at the elevated temperatures.

The distribution of some of the products of the reaction are shown in Figures 6.5 to 6.19 inclusive, depicting the effects of residence times, temperatures and hydrocarbon to oxygen ratios. All results are plotted as yield vs residence time. The yield of any component is expressed as moles component formed per mole n-butane reacted.

For any run, the carbon monoxide formation increases with residence times, while the carbon dioxide formation goes through a maximum. The larger amount of carbon dioxide during the induction period may be due to heterogeneous reaction at the surface of the reactor(49). The maximum yield of carbon monoxide at the reactor exit is 0.25 and 0.35 lb-mole/lb-mole n-butane reacted for runs at 687 and 702°F, respectively as shown in Figure 6.5. The carbon dioxide is almost constant at 0.027. Thus an increase in CO/CO_2 ratio is obtained at increased starting temperature. This effect of temperature has also been observed by other researchers(50). No significant effect was discernible for the hydrocarbon to oxygen ratios, as shown in Figure 6.13.

The formation of hydrogen, methane and ethane increased with residence times for all the runs. These were dependent on the initial temperature in so far as the initial temperature distribution is concerned, because of the influence of temperature on the induction period, as shown in Figure 6.6. However, the final amounts of these products were dependent on the hydrocarbon ratios. Figure 6.14 shows that the methane concentrations at the reactor exit are 0.22 and 0.10 for ratios of 7.7 and 13.9, respectively. The corresponding figures for ethane are 0.07 and 0.04.

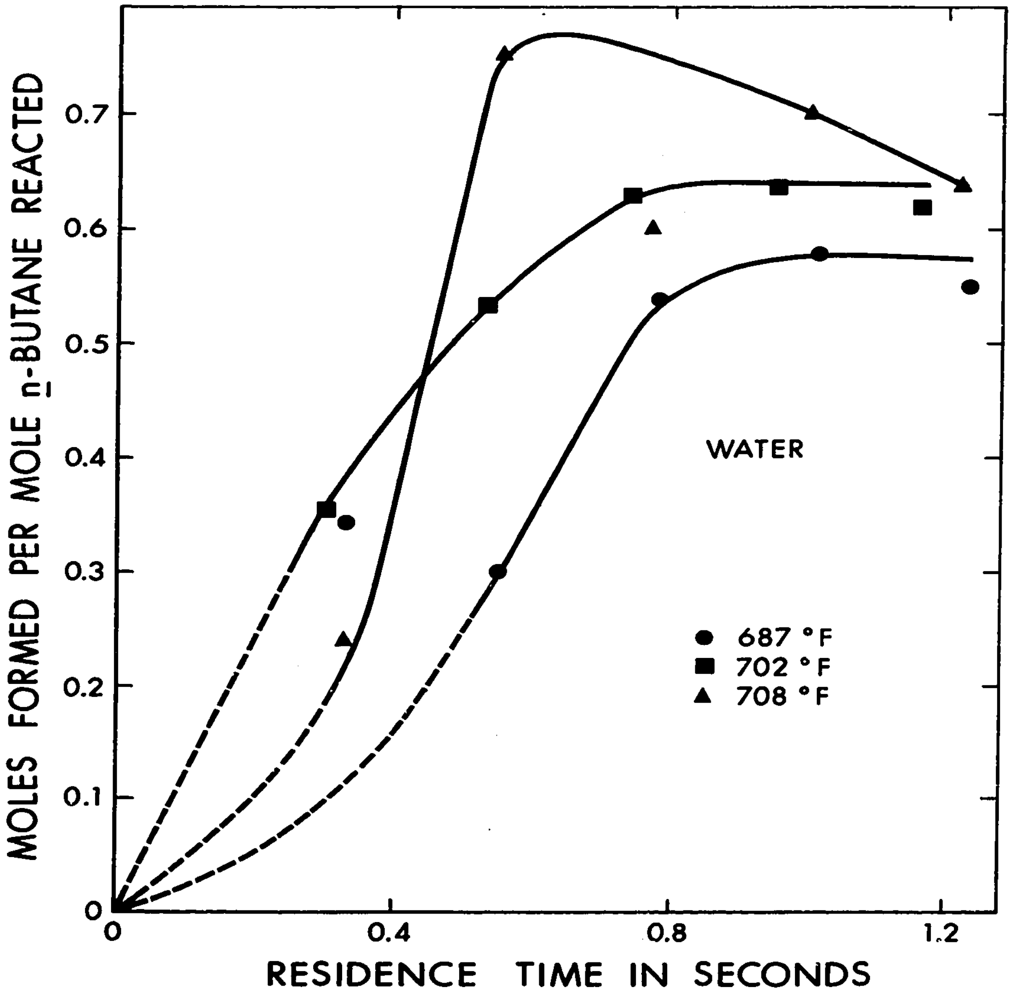


FIGURE 6.10 SELECTIVITY OF WATER - EFFECT OF INLET TEMPERATURE

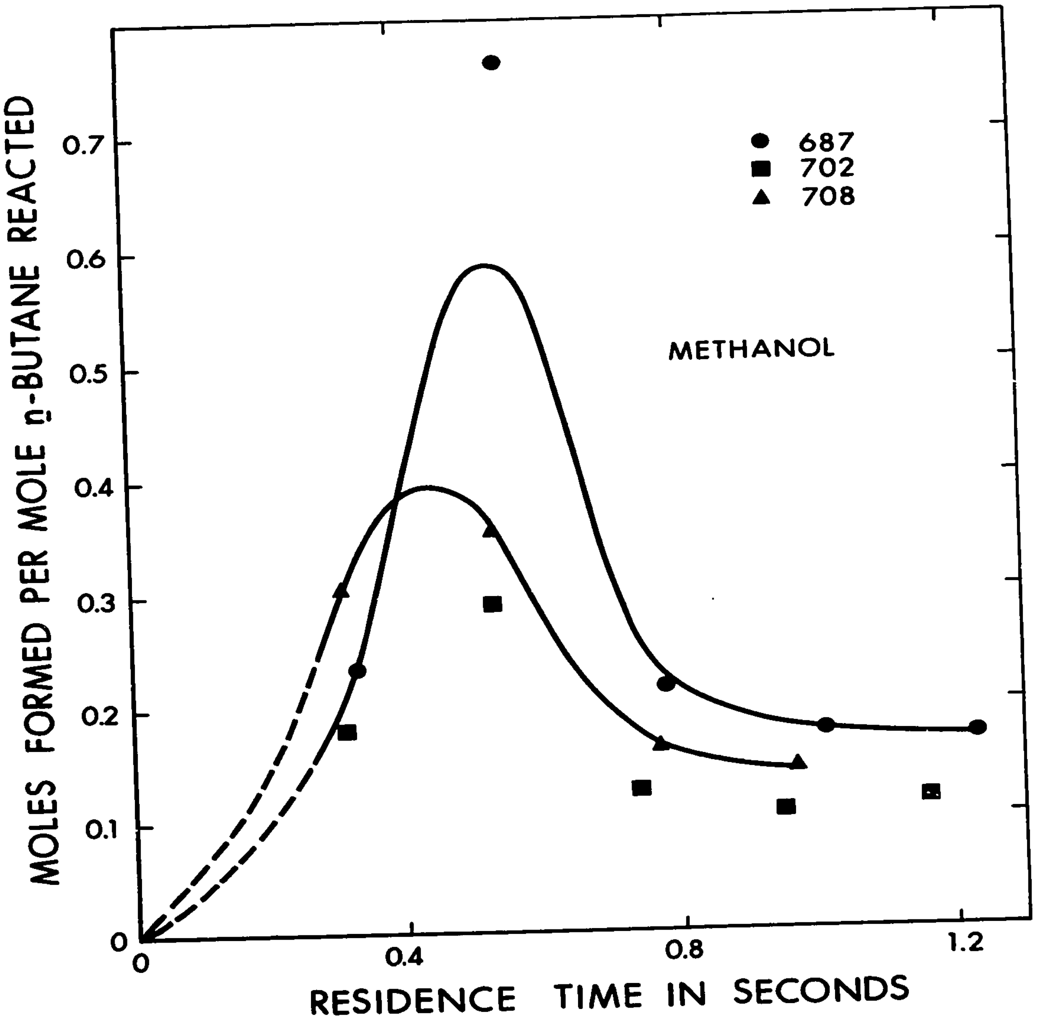


FIGURE 6.11 SELECTIVITY OF METHANOL - EFFECT OF INLET TEMPERATURE

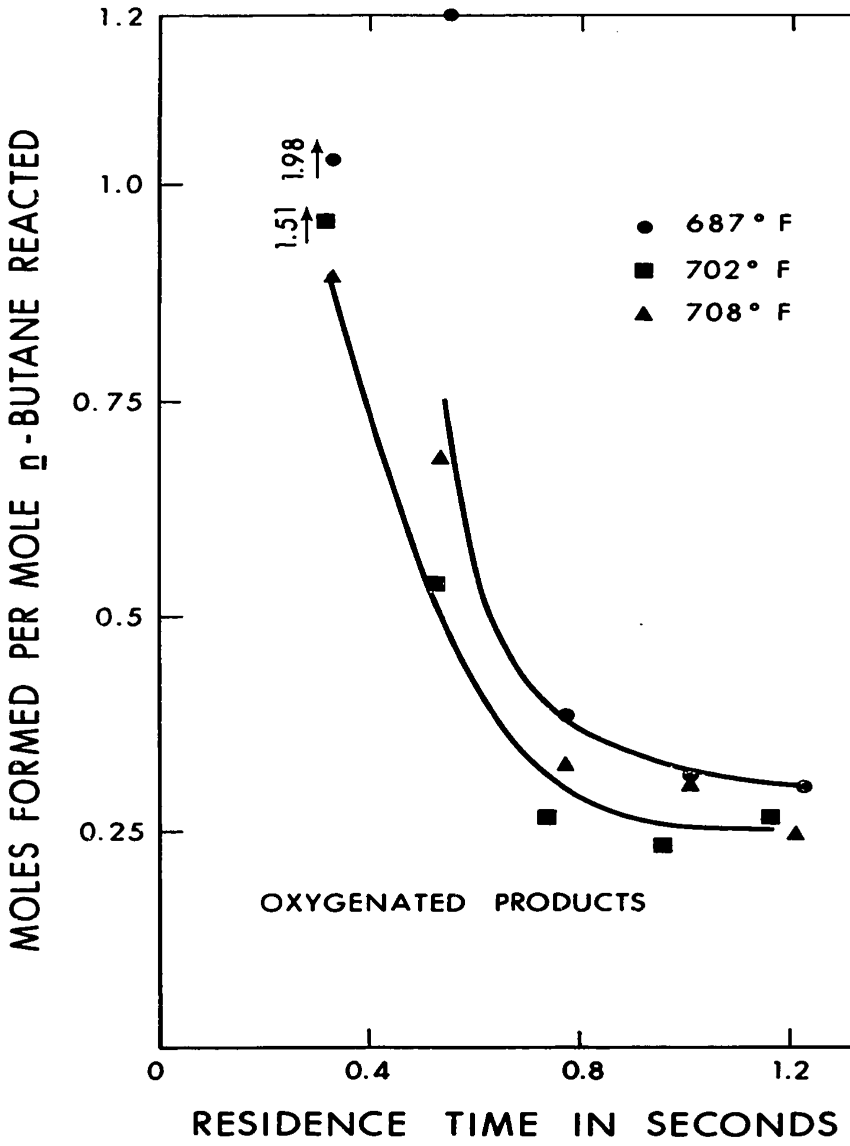


FIGURE 6.12 SELECTIVITY OF OXYGENATED PRODUCTS - EFFECT OF INLET TEMPERATURE

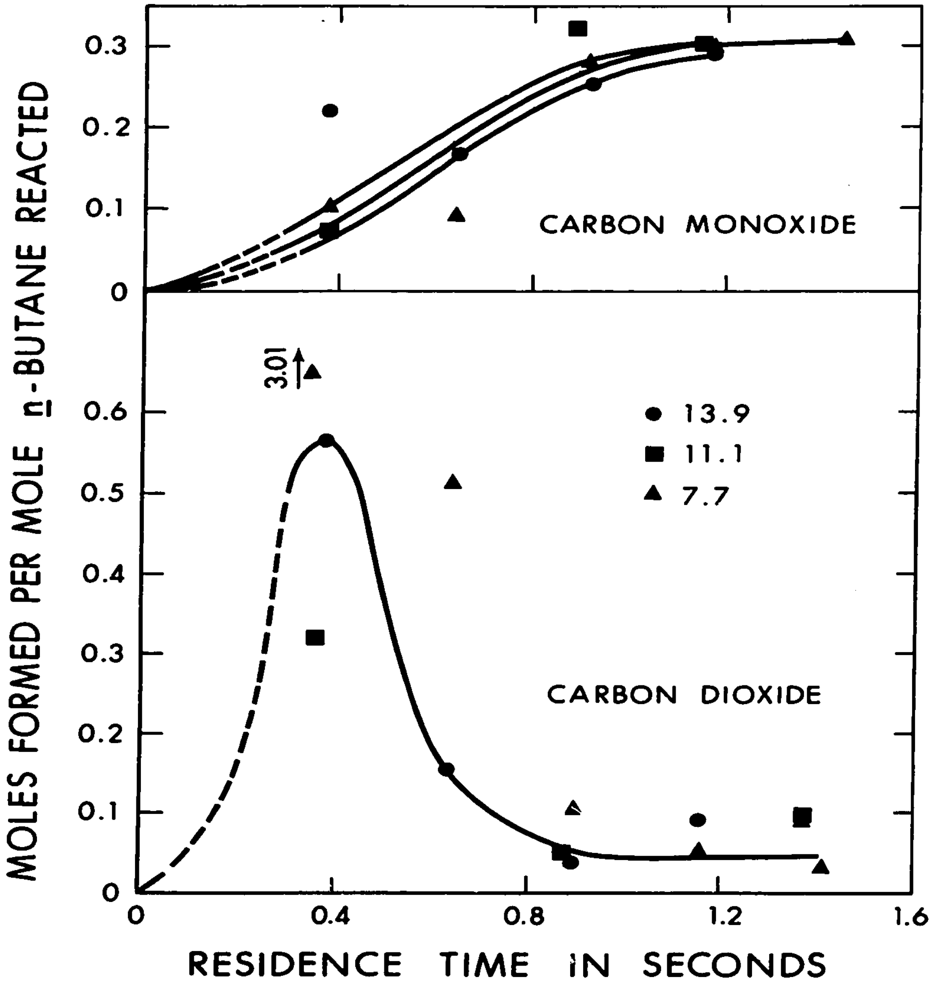


FIGURE 6.13 SELECTIVITY OF CARBON MONOXIDE AND CARBON DIOXIDE - EFFECT OF INLET MOLAR RATIO

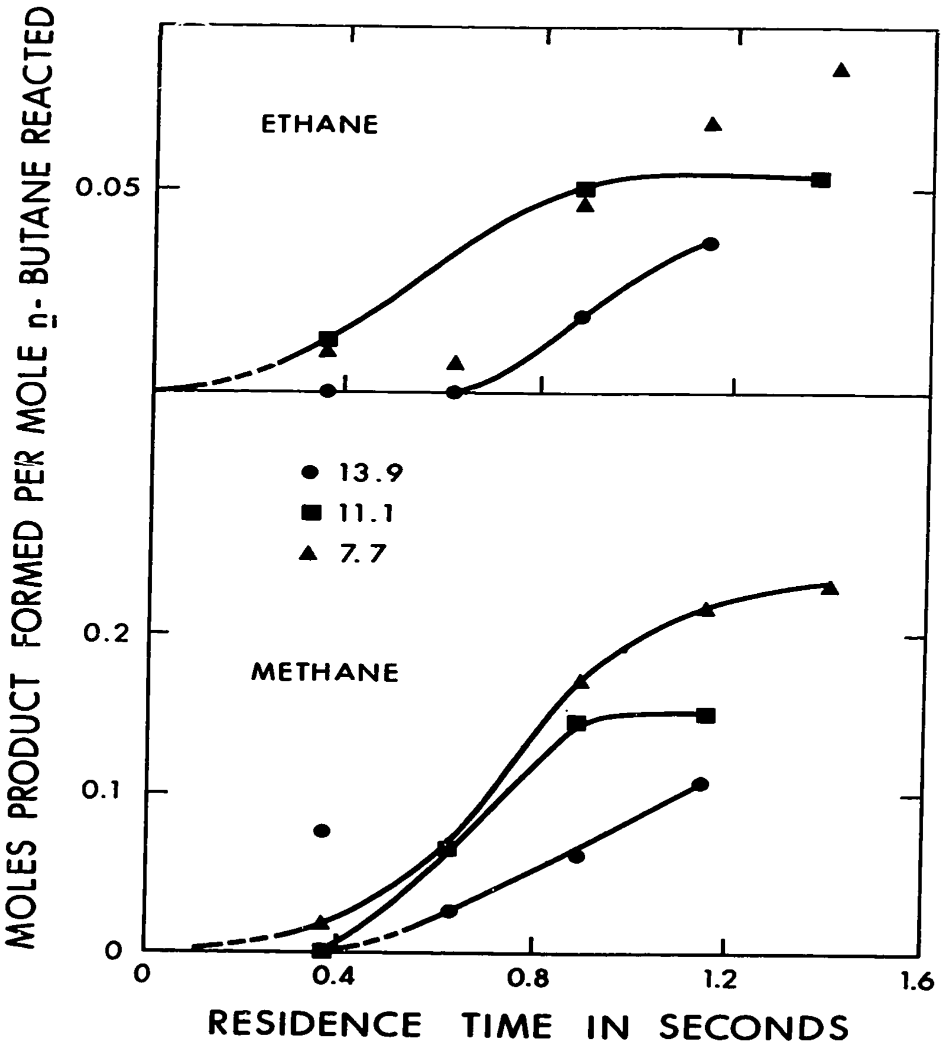


FIGURE 6.14 SELECTIVITY OF METHANE AND ETHANE - EFFECT OF INLET MOLAR RATIO

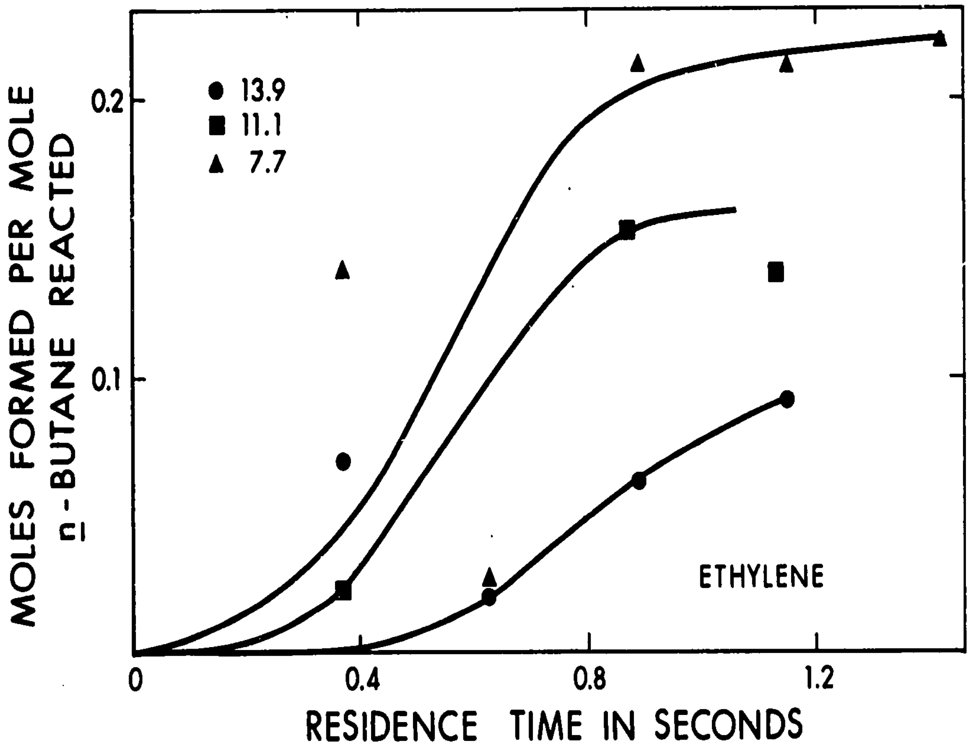


FIGURE 6.15 SELECTIVITY OF ETHYENE - EFFECT OF INLET MOLAR RATIO

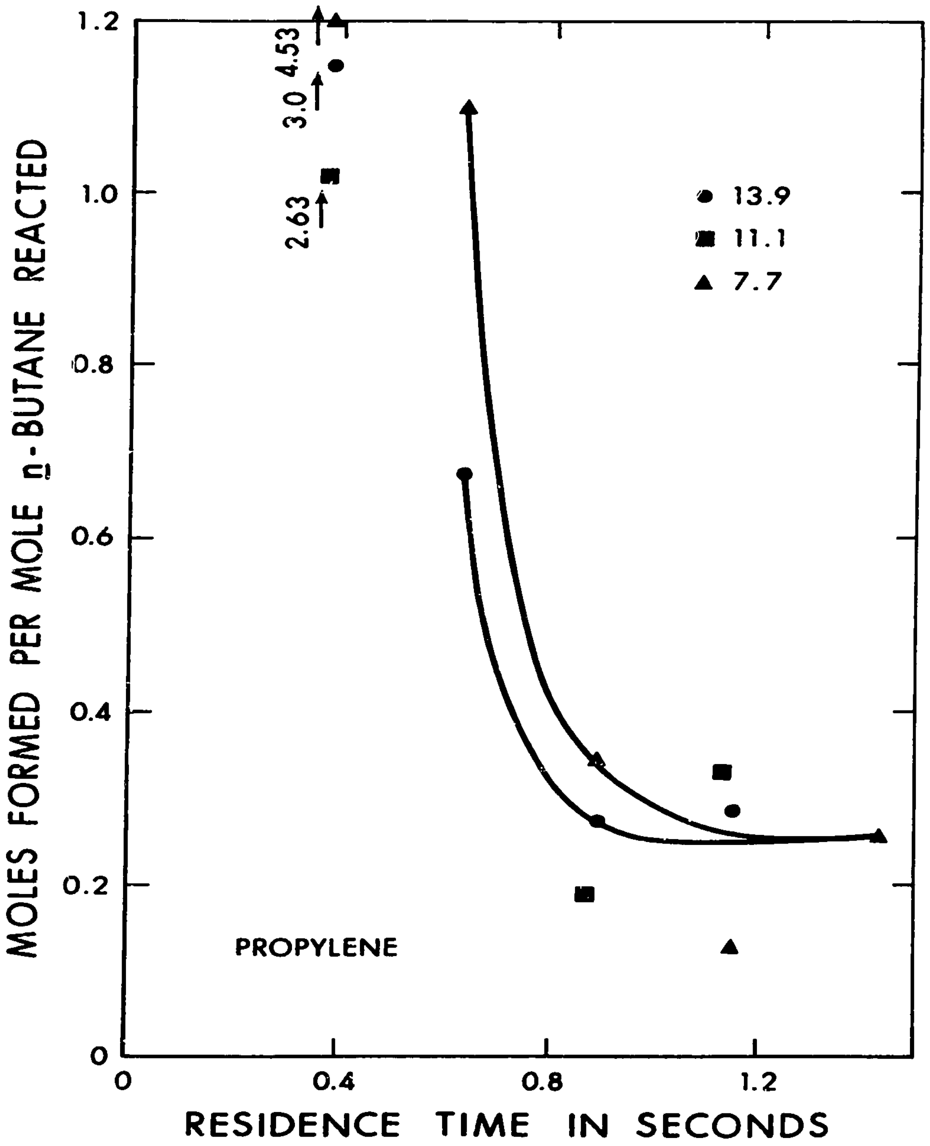


FIGURE 6.16 SELECTIVITY OF PROPYLENE - EFFECT OF MOLAR RATIO

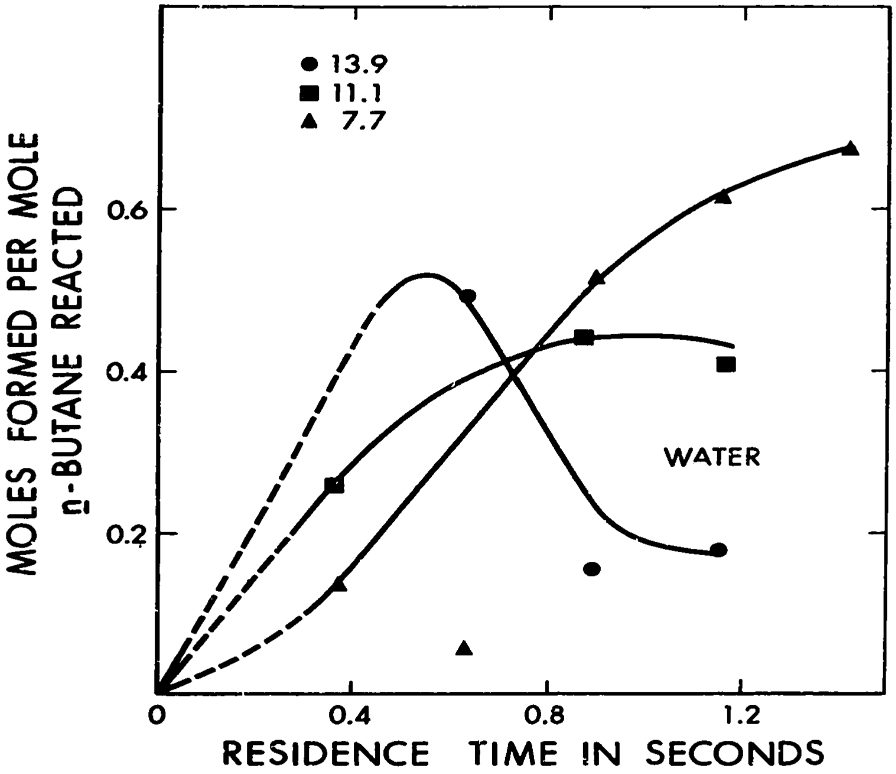


FIGURE 6.17 SELECTIVITY OF WATER - EFFECT OF INLET MOLAR RATIO

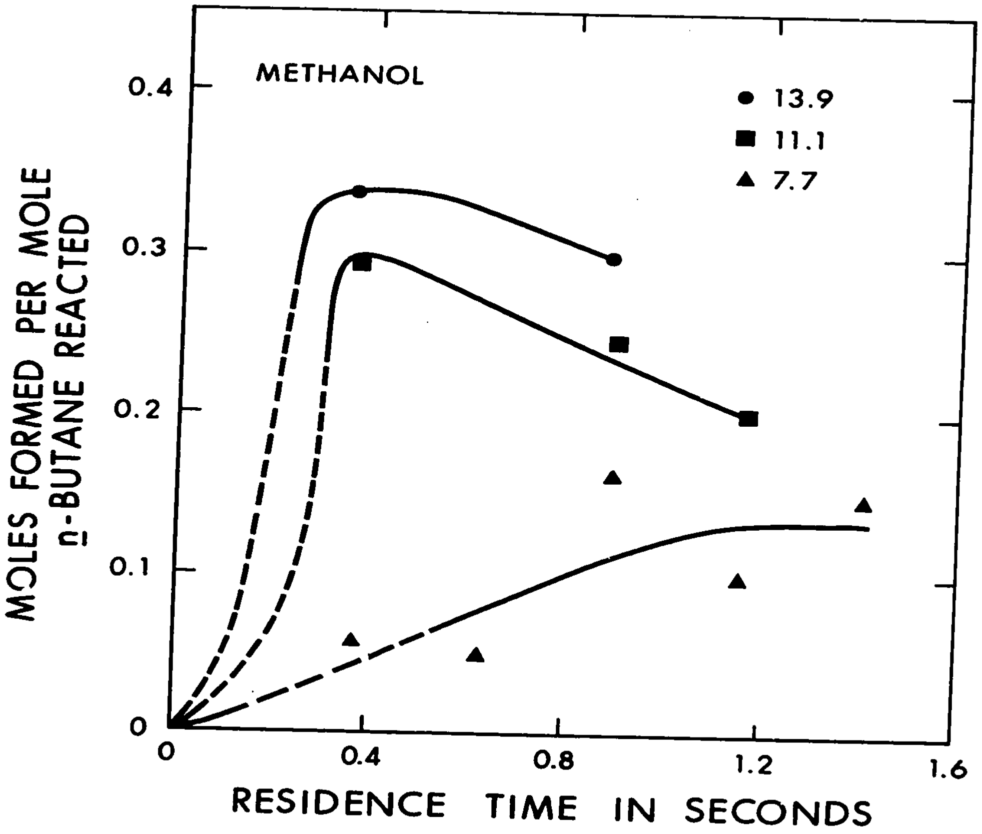


FIGURE 6.18 SELECTIVITY OF METHANOL - EFFECT OF MOLAR RATIO

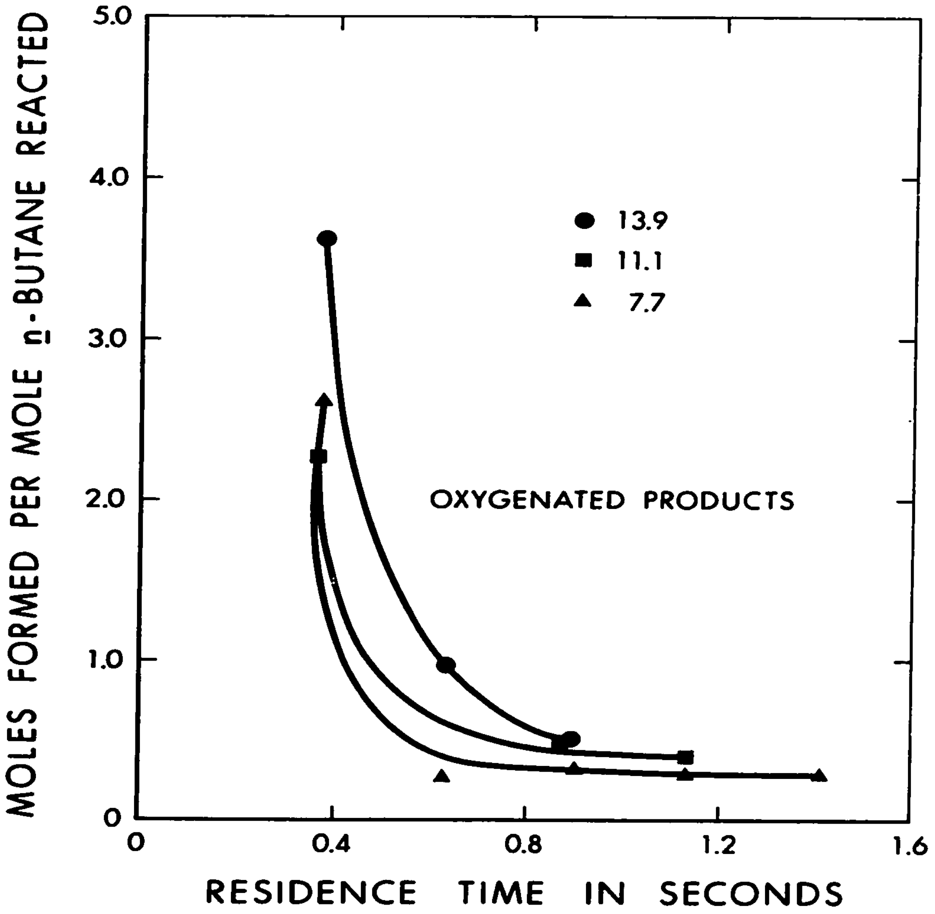


FIGURE 6.19 SELECTIVITY OF OXYGENATED PRODUCTS - EFFECT OF INLET MOLAR RATIO

Figures 6.7 to 6.9 and 6.15 and 6.16 show the olefin formation for different runs. The olefin formation except ethylene which increases, decreases with residence time. The high formation of propylene and n-butenes in the early stages of the reaction suggest that these are intermediate products and react further in the reactor. No definite trend could be observed for the olefins because of change in starting temperature and hydrocarbon ratios. The exit concentration is about 0.3 lb-mole/lb-mole n-butane reacted.

The ethylene concentration is affected by temperature and hydrocarbon to oxygen ratio. It rises from 0.175 at 687°F to 0.225 at 708°F, and 0.08 at ratio 13.9 to 0.225 at ratio 7.7.

The formation of methanol passed through a maximum for most of the runs. The final amount is little affected by the starting temperature, being about 0.15 lb-mole/lb-mole n-butane reacted (Figure 6.11). The amount rises to 0.3 lb-mole for the run at ratio of 13.9 (Figure 6.18).

The overall yield of oxygenated products decreases with residence time, and does not depend much on the starting temperature. The yield for the run at ratio 7.7 is 0.3 while it is 0.43 for the run at ratio of 13.9 (Figures 6.12 and 6.19).

Water formation increased with the extent of the reaction, reaching a maximum of about 0.6 to 0.65 at the reactor exit. The concentration was slightly dependent on the inlet temperature and hydrocarbon ratio (6.10 and 6.17). The decrease in water for the run at ratio 13.9 may be due to poor water analysis.

The large increase in temperature during the progress of the reaction makes interpretation of the plots very difficult, both because of the complicating effect of the temperature on the course of the reaction and because of the increased sensitivity of the different quantities in the figures to small changes in the abscissa. For this reason, it was intended to observe the reaction at lower conversion when the rise in temperature was small. This was done for runs 60, 61 and 64 using the Figures 6.2, 6.4 and 6.19, using a residence of 0.65 seconds which is before the steep part of the temperature profile.

Table 6.3 shows the amount of oxygenated products and the conversions of n-butane at a residence time of 0.65 for runs 60, 61 and 64.

TABLE 6.3

Run No.	Oxygenated Compounds	Conversion of n-Butane
60	0.87	2.0
61	0.61	3.0
64	0.36	4.5

Table 6.4 shows the residence time and oxygenated products formed at a fixed conversion of 3.5 per cent n-butane for the same runs. The maximum temperature rise for each run is also given.

TABLE 6.4

Run No.	Residence Time Sec.	Oxygenated Products	Maximum Temperature Rise °F
60	0.70	0.74	230
61	0.66	0.60	263
64	0.62	0.385	335

These results are plotted in Figures 6.20 to 6.23. Figure 6.20 shows that the conversion of n-butane is linear with the hydrocarbon to oxygen ratio, an observation similar to that obtained by Jones et al(29).

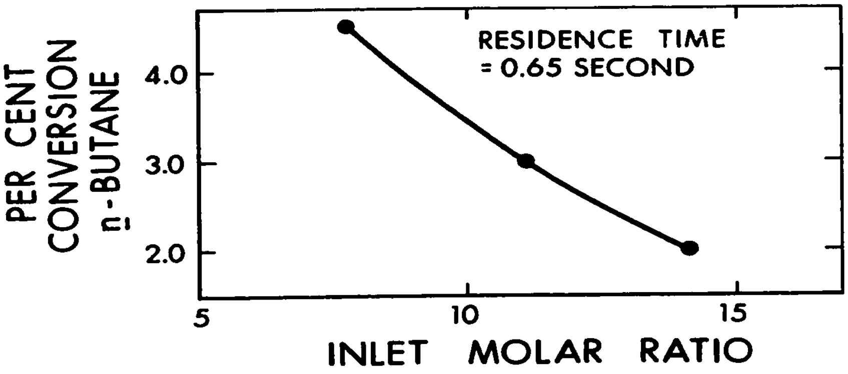


FIGURE 6.20 EFFECT ON n-BUTANE CONVERSION

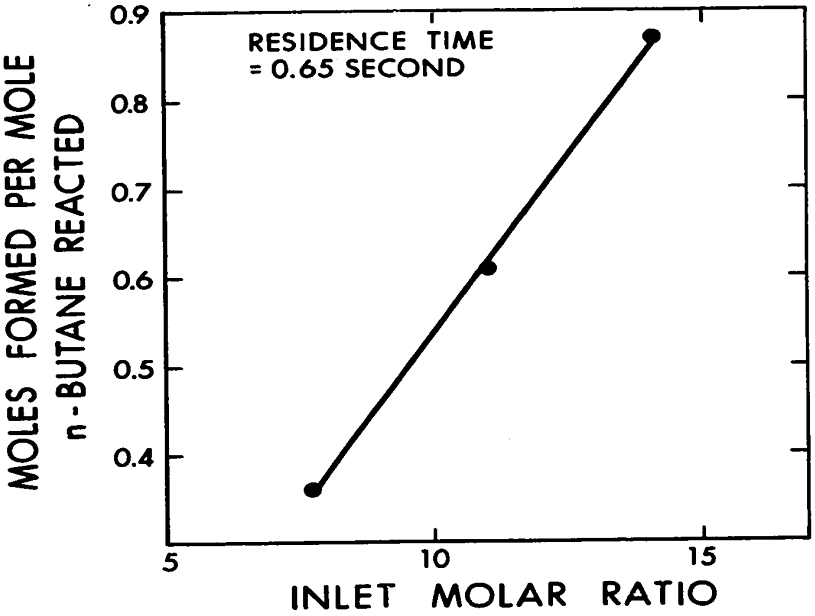


FIGURE 6.21 EFFECT ON SELECTIVITY OF OXYGENATED PRODUCTS

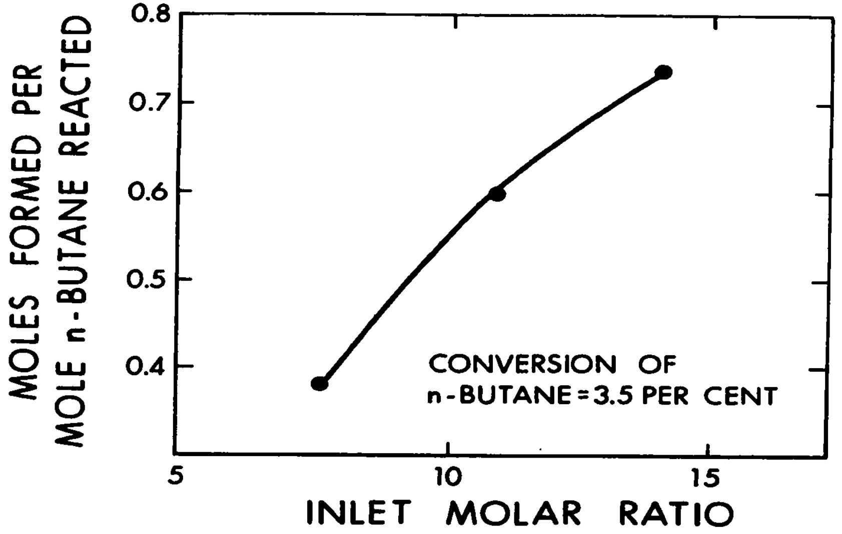


FIGURE 6.22 EFFECT ON SELECTIVITY OF OXYGENATED PRODUCTS

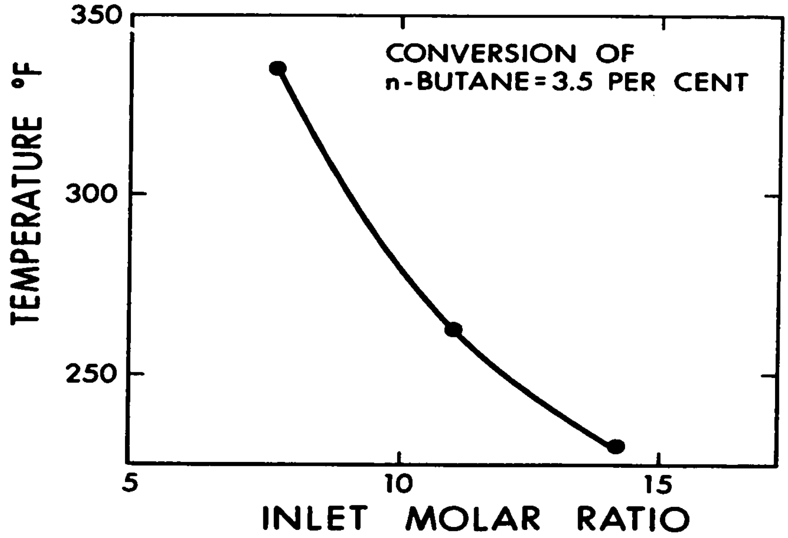


FIGURE 6.23 EFFECT ON MAXIMUM TEMPERATURE RISE

Figure 6.21 shows that the amount of oxygenated products rises sharply with decrease in the amount of oxygen in the system. Figure 6.22 shows that at a fixed conversion of 3.5 per cent n-butane, the amount of oxygenated products is much higher for a run at ratio of 13.9 compared to a run at lower ratios. The maximum temperature rise has already been noted to depend on the hydrocarbon to oxygen ratio. This dependence is shown in Figure 6.23 to be almost linear. The agreement of Figures 6.20 to 6.23 to the generally accepted behaviour of the hydrocarbon oxidation reaction lend support to the general nature of the curves drawn in Figures 6.2, 6.4 and 6.19.

6.5 Reaction Mechanism

The distribution of the products of the reaction with residence time and the effects of the operating variables on the distribution can give important clues as to the mechanism of the reaction. A knowledge of the mechanism would enable better choice of variables and other reactor parameters and would lead to better reactor design and process economy.

One very interesting mechanism proposed for the reaction is that by Knox(9) for the oxidation of propane. He obtained 80% of the initial products of oxidation as propylene, according to the reaction

$$C_3\dot{H}_7 + O_2 \rightarrow C_3H_6 + H\dot{O}_2$$

However, this result was not obtained by several other investigators (11,51,52). In the case of n-butane in the present study, not only butenes, but also large amounts of propylene are obtained as major initial products. This can be readily taken into account by the isomerization scheme of Semenov(2) and Shtern(8), as discussed in section 2.2. This, at the same time, explains the formation of a large amount of formaldehyde, acetaldehyde and methanol in the reaction products in the early stages.

The larger alkoxy radicals formed in the isomerization reaction scheme would likely break up and subsequently form paraffin by reacting with n-butane. The methoxy radical, at the lower temperatures, will form methanol by abstracting a hydrogen atom from the n-butane molecule. As the temperature rises, there will likely be a competing cracking route and hence the maximum in the formation of methanol will occur. In addition, methanol itself can get oxidized at the high temperatures reached in this study. Norrish and Porter(41) obtained appreciable secondary oxidation of methanol during the oxidation of n-butenes.

The role of aldehydes is now relatively well established. Salooza(53) found that acetaldehyde is the most reactive aldehyde and the reactivity does not increase with increase in the carbon chain length, as is the case with hydrocarbons. Formaldehyde was found to be far less reactive compared to others. However, in the present case, since the reaction condition is quite severe, all the aldehydes are likely to take part in the reaction. This is borne out by the experimental results which show a steep decrease in the amount of aldehydes at the end of the induction period.

The yield of propylene and n-butenes decrease sharply in the same pattern as aldehydes. The yield of ethylene only increases with reaction. This strongly suggests a pivotal role being played by olefins, as suggested by Knox. At the temperature of this study, ethylene does not enter into the reaction, but propylene and n-butenes may do so in accordance with the mechanism of Knox. A relatively large amount of ethylene oxide and propylene oxide found in the initial products lends further evidence to this postulate. Accordingly, a mechanism combining the isomerization scheme and the olefin scheme may be advanced to explain the hydrocarbon oxidation reaction. However, it would not be possible at this stage to make any definitive conclusions in this regard. More experimental data, and especially experimental studies of the elementary steps of the reaction are essential to establish the mechanism of the partial oxidation reaction.

6.6 Reactor Modelling

6.6.1 Simplified Kinetic Models

In absence of a known reaction mechanism and because of the complexity of the hydrocarbon oxidation reaction, attempts have been made to develop a suitable kinetic scheme which can be used for reactor design purposes. Several different mechanisms were postulated, but the following two mechanisms were studied in some detail.

Mechanism I.

1) $RH + O_2 \rightarrow \dot{R} + H\dot{O}_2$ (6.1)
2) $\dot{R} + O_2 \rightarrow A = B + H\dot{O}_2$ (6.2)
3) $\dot{R} + O_2 \rightarrow R'CHO + \dot{O}H$ (6.3)
4) $A = B + 2H\dot{O}_2 \rightarrow 2\dot{O}H + AO + BO$ (6.4)
5) $R'CHO + O_2 \rightarrow RC\dot{O} + H\dot{O}_2$ (6.5)
6) $RC\dot{O} + O_2 \rightarrow$ Products (6.6)
7) $RH + \dot{O}H \rightarrow \dot{R} + H_2O$ (6.7)
8) $\dot{R} + O_2 \rightarrow$ Termination (6.8)
9) $RH \rightarrow$ Products (6.9)

RH in the above equations stand for hydrocarbon, A = B for olefins and R'CHO for the aldehydes. The mechanism in essence is a simplified version of a combination of the Semenov scheme and the Knox scheme.

The rate equations for the different species can be obtained by applying the principle of stationary state approximation(54), a method quite commonly used in chain kinetics. The a's in the equations below for the concentration of the free radicals are rate constants multiplied by the concentration of the molecular species involved.

$$[R\dot{C}O] = \frac{a_5}{a_6} \tag{6.10}$$

$$[\ \dot{R}\ ] = \frac{2a_1 + a_5}{a_8} \tag{6.11}$$

$$a_7[\dot{O}H] = \frac{(a_2 + a_3)(2a_1 + a_5)}{a_8} + a_1 + a_5 \tag{6.12}$$

$$2a_4[H\dot{O}_2]^2 = a_1 + a_5 + \frac{a_2}{a_8}(2a_1 + a_5) \tag{6.13}$$

Denoting the concentrations of RH, O_2 and R'CHO by C_A, C_B and C_C, respectively and on simplification,

$$-\frac{dC_A}{dt} = 2K_1C_AC_B + K_5C_BC_C + \frac{K_2+K_3}{K_8}(2K_1C_AC_B + K_5C_BC_C) + K_9C_A \tag{6.14}$$

$$-\frac{dC_B}{dt} = 3K_1C_AC_B + 3K_5C_BC_C + \frac{K_2+K_3}{K_8}(2K_1C_AC_B + K_5C_BC_C) \tag{6.15}$$

$$\frac{dC_C}{dt} = \frac{K_3}{K_8}(2K_1C_AC_B + K_5C_BC_C) - K_5C_BC_C \tag{6.16}$$

Mechanism II

1) $$RH + O_2 \rightarrow \dot{R} + H\dot{O}_2 \tag{6.17}$$

2) $$\dot{R} + O_2 \rightarrow Q + \dot{M} \tag{6.18}$$

3) $$\dot{R} + O_2 \rightarrow P + \dot{M} \tag{6.19}$$

4) $$P + O_2 \rightarrow \dot{N} + \dot{M} \tag{6.20}$$

5) $$RH + \dot{M} \rightarrow \dot{R} + S \tag{6.21}$$

6) $$\dot{M} \rightarrow \text{Termination} \tag{6.22}$$

7) $$RH \rightarrow \text{Products} \tag{6.23}$$

In the above reaction equations, Q and S represent end products, P is an intermediate responsible for branching and $\dot{N}$ and $\dot{M}$ are free radical species. On simplification, the rate equations in this case become:

$$-\frac{dC_A}{dt} = K_1 C_A C_B + \frac{K_5}{K_6} C_A \left(2K_1 C_A C_B + K_4 C_B C_C\right) + K_7 C_A \tag{6.24}$$

$$-\frac{dC_B}{dt} = 2K_1 C_A C_B + K_4 C_B C_C + \frac{K_5}{K_6} C_A \left(2K_1 C_A C_B + K_4 C_B C_C\right) \tag{6.25}$$

$$\frac{dC_C}{dt} = \left[K_1 C_A C_B + \frac{K_5}{K_6} C_A \left(2K_1 C_A C_B + K_4 C_B C_C\right)\right] / \left(1 + \frac{K_2}{K_3}\right) - K_4 C_B C_C \tag{6.26}$$

The reactor temperature profile is given by

$$\frac{dT}{dz} = \frac{1}{mC}\left[- 4 \frac{hw}{D_r} (T - T_w) + \sum_{i=1}^{n} r_i \, \Delta H_i\right] , \tag{6.27}$$

which incorporates the heat of reaction terms. n in the above equation is the number of reaction steps in the mechanism involved.

The rate constants are related to the temperature by the Arrhenius relation:

$$K_i = A_i' e^{-E_i/RT} \tag{6.28}$$

where A_i' is the frequency factor and E_i the activation energy for the reaction.

6.6.2 Estimation of Parameters

The estimation of the parameters in a nonlinear kinetic model poses a severe problem. Several methods have been suggested in literature. Kittrel et al(55) applied iterative nonlinear least squares regression techniques to obtain parameters for heterogeneous kinetic systems. Donnelly and Quon(56) employed the method of quasilinearization which reduced the system to a system of linear boundary value equations. Ball and Groenweghe(57) employed a method proposed by Marquardt(58) who attempted to combine the best features of Gauss-Newton and the steepest descent methods. The Gauss-Newton method is characterized by quadratic convergence when sufficiently close to the final solution point. The steepest descent method works no matter how far away the solution point is, but becomes very slow as the solution point approaches. The proper combination of these methods would thus appear very desirable and would likely give rapid convergence with a desirable lack of sensitivity to initial values of the parameters.

The parameters of the models in the present case are poorly known and the steepest descent method appeared the likely choice for preliminary estimation. A number of variations of the classical method have been used by several authors and the one by Rosenbrock(59) was adopted in the present work. The essence of the method is to vary one parameter at a time and then find out the best direction of advance and continue the iterations. The step size is very simply controlled by observing the change in the quantity to be minimized or maximized. The programming is simple and is aptly described by Rosenbrock(60).

In the actual programming, the pre-exponential factor was modified as

$$A_i' = 10^{-4} \exp (A_i) \quad , \qquad (6.29)$$

and the Arrhenius equation was written in the form

$$K_i = 10^{-4} \exp (A_i - E_i'/T) \quad , \qquad (6.30)$$

where $E_i' = \frac{E_i}{R}$.

The rate equations were expressed in terms of conversion rather than concentration and the dependence on time was changed to dependence on the length of the reactor. The temperature was normalized by dividing by a base temperature. Denoting the moles of hydrocarbon, oxygen and the intermediate as N_A, N_B and N_C, the conversions of the components are defined as follows:

For the hydrocarbon,

$$X_A = \frac{N_{A_o} - N_A}{N_{A_o}} \qquad (6.31)$$

where N_{A_o} is the initial moles of the hydrocarbon.

For oxygen

$$X_B = \frac{N_{B_o} - N_B}{N_{B_o}} \qquad (6.32)$$

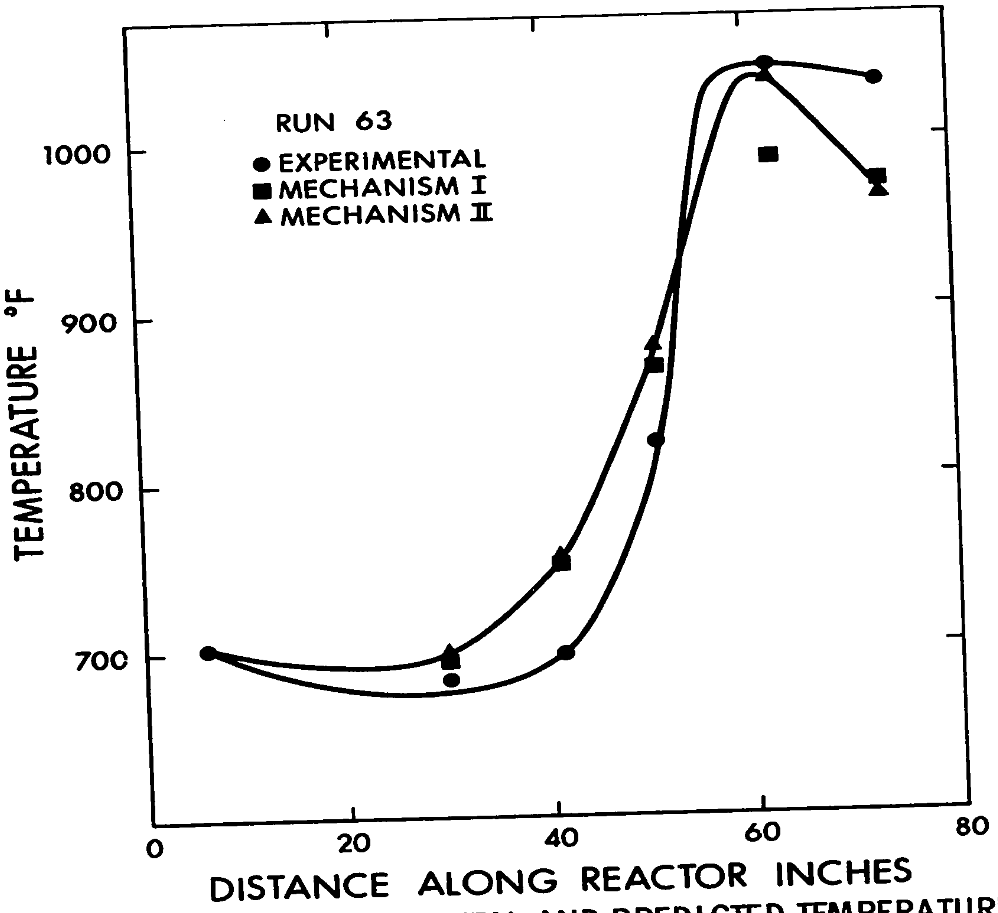


FIGURE 6.24 EXPERIMENTAL AND PREDICTED TEMPERATURE PROFILES

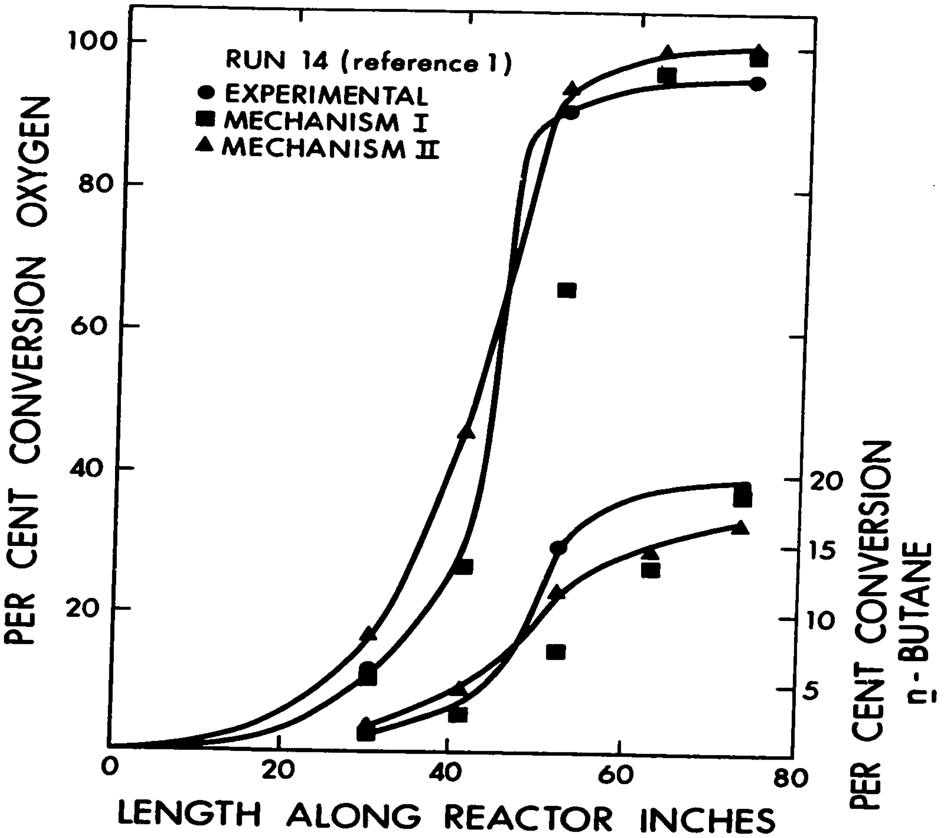


FIGURE 6.25 EXPERIMENTAL AND PREDICTED CONVERSIONS

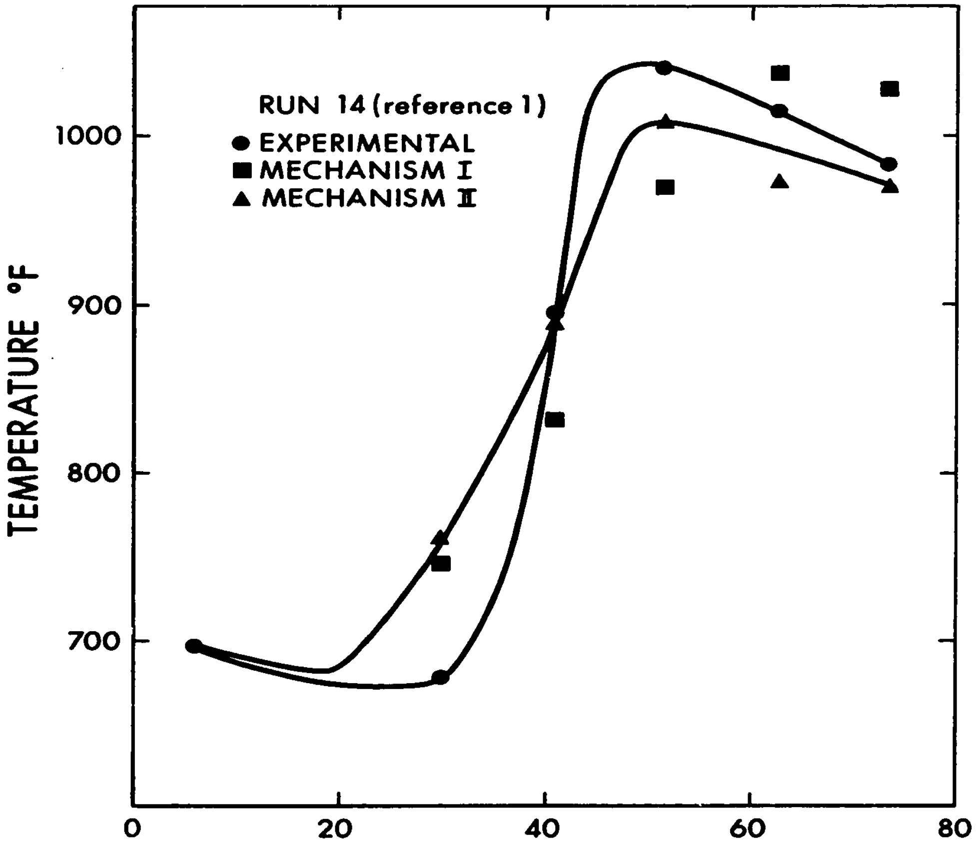


FIGURE 6.26 EXPERIMENTAL AND PREDICTED TEMPERATURE PROFILE

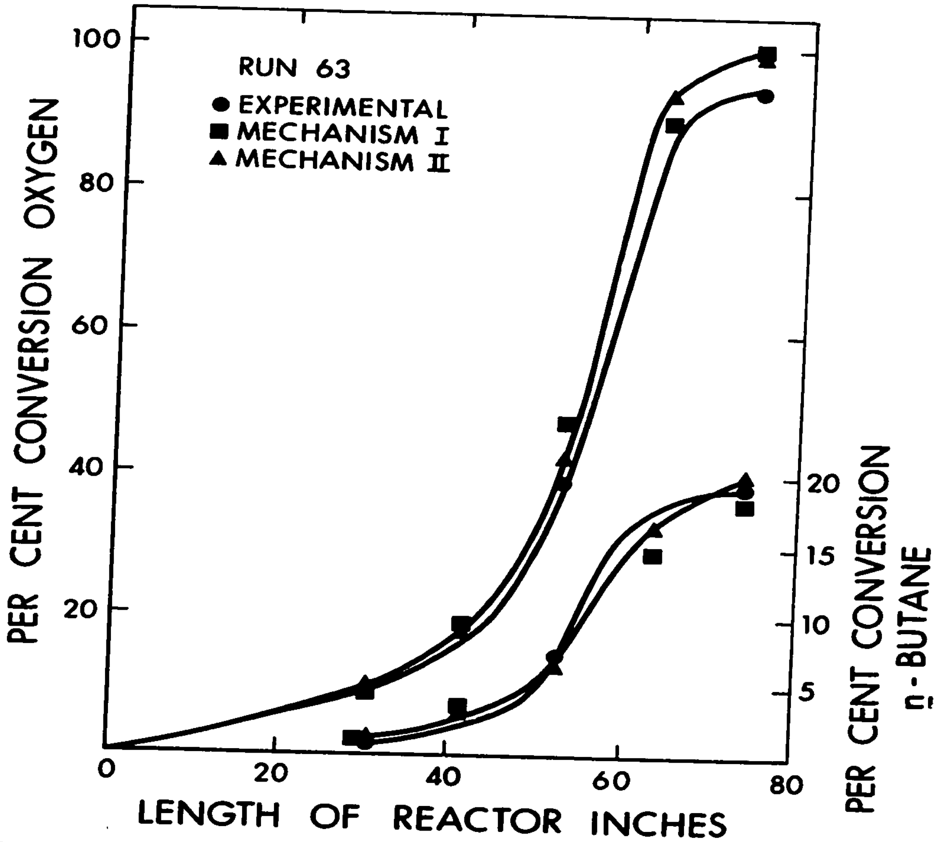


FIGURE 6.27 EXPERIMENTAL AND PREDICTED CONVERSIONS

where N_{B_o} is the initial moles of oxygen.

For the intermediate component, the conversion can be expressed in terms of the hydrocarbon or oxygen. In terms of hydrocarbon, this is

$$X_C = \frac{N_C}{N_{A_o}} \qquad (6.33)$$

The unknown parameters in the two models can now be estimated using the experimental data available for the overall conversions of _n_-butane and oxygen and the temperature profile of the gas. However, on inspection of the two models, there are about twenty or so unknowns in each of them. Simultaneous treatment of such a large number of unknowns is impractical. In order to circumvent this problem, the values available in literature on the different parameters are chosen and the number of unknown parameters is brought down to three or four. Next, a sequential approach is adopted, i.e., the system is solved for three or four unknowns and then another set of unknown parameters are chosen, and so on.

The computer program is general for both the mechanisms. The slope subroutine has to be supplied in each case. Data for experimental runs 60, 62 to 66 and 68 were used in the analysis. Figures 6.24 to 6.27 present the temperature profiles and the conversions as obtained from the models for two runs and compared with the experimental values. Table 6.5 gives the final values of the parameters for the two mechanisms. The parameter values with asterisks were estimated.

TABLE 6.5

Parameter Values of Mechanisms I and II

	Mechanism I			Mechanism II		
Reaction Number	A	E/1000 Btu/lb-mole	$\frac{\Delta H}{1000}$ Btu/lb-mole	A	E/1000 Btu/lb-mole	$\frac{\Delta H}{1000}$ Btu/lb-mole
1	35.0	50.07*	-70.0	34.47*	50.04*	-75.0
2	34.06*	25.0	20.0	$A_2 - A_3$ = 0.0	$E_3 - E_2$ = -5.2*	60.0
3	34.0	27.0	69.8*			70.0
4	-	-	15.0	34.07*	30.44*	-60.0
5	35.0	30.98*	-60.0	$A_5 - A_6$ = 10.0	$E_6 - E_5$ = -9.6*	40.9*
6	-	-	50.0			-15.5*
7	-	-	33.5*	34.68*	53.17*	-40.0
8	34.0	40.0	40.0			
9	35.0	54.02*	0.0			

Table 6.6 gives the variance covariance matrix for three parameters in mechanism II. The parameters considered were the activation energies for the initiation step, the branching step and the overall cracking step -- reactions 1, 4 and 7, respectively. Data for runs 62 to 66 were used to calculate this matrix.

TABLE 6.6

Parameter Estimates: $E_1 = 50.04$ $E_4 = 30.44$ $E_7 = 53.17$

Variance Covariance Matrix

$$\underline{C} = \begin{bmatrix} 1.4142 & -.6966 & -.2857 \\ -.6966 & .3459 & .1384 \\ -.2857 & .1384 & 1.9675 \end{bmatrix}$$

TABLE 6.7

Variance and Standard Deviation

Runs	Mechanism	Variance			Standard Deviation		
		n-butane conversion	oxygen conversion	Temperature $T^* = \frac{T}{1185}$	n-butane conversion	oxygen conversion	Temperature T
Homogeneous Runs	I	5.68×10^{-4}	1.59×10^{-2}	2.71×10^{-3}	0.024	0.126	61.5
	II	4.86×10^{-4}	1.21×10^{-2}	2.01×10^{-3}	0.022	0.110	53.0
Transported Bed Runs*	I	1.0×10^{-3}	3.78×10^{-2}	2.93×10^{-3}	0.0316	0.194	63.7
	II	5.45×10^{-4}	2.34×10^{-2}	9.36×10^{-4}	0.0233	0.152	36.2
Independent Runs**	I	1.40×10^{-3}	4.47×10^{-2}	3.20×10^{-3}	0.0384	0.211	66.8
	II	2.73×10^{-4}	1.31×10^{-2}	3.61×10^{-3}	0.0165	0.114	71.5

* To be dealt with in section 7.4.

** Reference 1.

The two models were also used to predict the temperature profiles and conversions for a number of runs made by Anderson(1) earlier in this laboratory. The runs used from his results were runs 11, 12, 13, 14 and 17. Table 6.7 shows the variance and standard deviation for the present runs and the runs by Anderson for n-butane conversion, oxygen conversion and temperature profile. It is seen that for the present runs, there is a slight edge of mechanism II compared to mechanism I. For the other set of runs, mechanism II is considerably better than mechanism I. The two sets of data above cover a range of starting temperatures from 680°F to 708°F and starting n-butane to oxygen ratios of 14.0 to 7.0. The predictions by the two models in this fairly large range of operating conditions have been quite good. This, however, does not mean that either mechanism is taking place in the reactor. The establishment of a mechanism of the reaction is a much larger problem and the present models are used only to predict the overall conversions and temperature profiles in the reactor under the operating conditions as stated.

6.7 Summary

The temperature profiles and overall conversions of n-butane and oxygen are consistent and agree with other results in this area. The product distribution data suggest that a combination of the aldehydic scheme of Semenov and Shtern and the olefinic scheme of Knox may be taking place in the reactor. However, the interpretation of all the data were difficult and were associated with considerable uncertainty because of the high sensitivity of the ordinate with a relatively small change in the abscissa in most of the cases.

An attempt has been made to develop a suitable kinetic scheme for the reaction. This attempt has been limited to the prediction of temperature profiles and overall conversions for the different runs. Two schemes have been given particular attention and their parameters obtained by a numerical method. The schemes have been tested against independent experiments in an earlier work and the two models, especially model II predict the temperature profiles and overall conversions quite well. The variance and standard deviation in each case are presented.

CHAPTER VII

TRANSPORTED BED REACTOR: RESULTS AND DISCUSSIONS

7.1 Introduction

A mathematical model for a transported bed reactor has been formulated and a numerical method developed to solve the problem. Effects of particle size and loading ratio on the gas and solid temperature profiles are investigated.

The performance of the transported bed reactor in the partial oxidation of n-butane with air is evaluated. The selectivity of different products are compared with those obtained in a homogeneous reactor. The effect of additional surface in a transported bed reactor is evaluated.

The kinetic models for the homogeneous reactor are used to predict the temperature profiles and conversions in the transported bed reactor.

7.2 Evaluation of Heat Transfer Characteristics

A preliminary study of the behaviour of a transported bed system was required to evaluate its heat transfer characteristics. This was done with particular emphasis on the effect of a radial variation in particle temperatures. In earlier studies on heat transfer in transport lines, the solids temperature has been considered uniform across the cross section(61). While it would be true for very small particles, the larger particles may have temperature variations large enough to affect the results.

Basic equations for momentum and heat transport for a gas solids system were developed by Soo et al(62,63). Efforts to take into account the velocity profiles of the solid particles and their concentration distributions were not conclusive(64) and it was assumed that these could be taken care of by lumped parameters. Experimental investigations of the heat transfer characteristics of a two phase system were made by Farbar and Depew(65) and Abel and coworkers(66). A general increase in the gas to wall heat transfer was reported for a gas-solids system. The particle diameter and the solids to gas loading ratios were the two main variables, but a satisfactory correlation was not available for a wide range. Studies of the drag coefficients for a particulate system has been made by several investigators; the results are not definitive, but suggest that standard drag coefficients for single spheres can be used for the transport system(67).

Practically no work has been reported in literature on the gas to solids heat transfer coefficients, mainly because of the experimental difficulties involved in such studies. In most heat transfer studies in gas solids systems, the temperature difference between the gas and solids was small and reliable measurement of this difference was not possible. Chukhanov(68) made an attempt to use the data for fixed spheres in a moving gas. The gas to solids heat transfer coefficient in this study was obtained from Gröber(69) and the gas to wall heat transfer coefficient was obtained from Farbar and Morley(70).

The following equations can be derived for the reactor system:

Continuity equations -- consideration of continuity for the gas phase only gives for a perfect gas

$$\frac{m}{A_r} = \frac{u}{v} = \frac{uP}{RT} \tag{7.1}$$

The concentration of the solid particles is given by

$$m_p = m_p{}^* \frac{u}{up} \quad , \qquad (7.2)$$

which accounts for the fact that higher velocity of the solid particles shows up as a decrease in concentration of the solids.

Overall energy equation -- consideration of heat transfer to the wall and the generation of heat because of the reaction leads to the equation, for one pound of gas;

$$d[CT + m_p C_p T_p] = - \frac{h_w A_w}{m} (T - T_w)dZ + \frac{\varepsilon A_r}{m} \sum_{i=1}^{n} r_i(-\Delta H_i)dZ \quad ,$$

which can be put in the form

$$\frac{dT}{dZ} = \frac{1}{mC} [-4 \frac{h_w}{D_r}(T - T_w) - h_c A_s (T - v_s) + \varepsilon \sum_{i=1}^{n} r_i(-\Delta H_i)] \ , \qquad (7.3)$$

where n is the number of rate equations.

Solids energy balance -- heat is received by the solids from the gas by convection:

$$d[m_p C_p T_p] = \frac{h_c A_s}{m} (T - v_s) \ dZ$$

$$\frac{dT_p}{dZ} = \frac{h_c A_s}{m_p C_p m} (T - v_s) \qquad (7.4)$$

Momentum of solid particles -- the solids are conveyed by the viscous drag exerted by the gaseous stream. The rate of change of momentum can be expressed as

$$g_c - F\ (u - u_p) = u_p \frac{d\ u_p}{dZ} \qquad (7.5)$$

where the time lag of fluid-solid motion (sec^{-1}) $F = \frac{3}{4} \frac{C_D}{d_p} \frac{\rho}{\rho_p} \left| u - u_p \right|$, and the drag coefficient are functions of the particle Reynolds number

$$Re_p = \frac{d_p \, |u-u_p| \rho}{\mu}$$

Overall momentum equation -- since the solid particles are driven by the gas, the momentum balance gives

$$\frac{dP}{\rho} + \frac{udu}{g_c} + \frac{m_p u_p du_p}{g_c} + \frac{2u^2 f}{g_c D_r} dZ + dZ \frac{\rho Ps}{\rho} = 0$$

Combining with the continuity equation and solids momentum equations leads to

$$\frac{du}{dZ} \left(\frac{1}{u} - \frac{u}{g_c RT}\right) = \frac{1}{T}\frac{dT}{dZ} + \frac{m_p u_p}{g_c RT}\frac{du_p}{dZ} + \frac{2u^2 f}{g_c RTD_r} + \frac{1}{g_c RT}\frac{\rho Ps}{\rho} \qquad (7.6)$$

Gas phase material balance -- material balance for a small increment of length dZ gives

$$\frac{dx_i}{dZ} = \frac{\varepsilon}{G_o y_o} r_i \quad \text{, where} \qquad (7.7)$$

$r_i = \xi(\underline{x},\underline{K},T)$, and is derived in appendix F. ε is the void fraction and is defined as

$$\varepsilon = 1 - \frac{\text{volume of solids}}{\text{total volume}}$$

$$= 1 - \frac{\text{volume of solids}}{\text{volume of gas}}$$

$$= 1 - \frac{w_p/\rho_p}{m/\rho}$$

$$= 1 - m_p \frac{\rho}{\rho_p} \qquad (7.8)$$

A_s is the solids surface area per ft reactor and is given by

$A_s = \pi d_p^2 \times N$, where N = no. of particles per ft reactor.

$$N = w_p \frac{\text{lb solid}}{\text{hr}} \frac{1}{u_p} \frac{\text{hr}}{\text{ft}} \frac{1}{\rho_p} \frac{\text{ft}^3}{\text{lb solid}} \frac{1}{1/6\ \pi\ d_p^3} \frac{1}{\text{ft}^3}$$

$$= \frac{6\ w_p}{u_p \rho_p d_p} \tag{7.9}$$

Combining equation (7.4) with the above gives,

$$\frac{dT_p}{dZ} = \frac{6\ h_c}{u_p \rho_p d_p C_p} (T - v_s) \tag{7.10}$$

Heat conduction equation into the solids -- the radial temperature distribution of the solid particles is given by

$$\frac{\partial v}{\partial t} = \frac{\alpha}{r_p^2} \frac{\partial}{\partial r_p} (r_p^2 \frac{\partial v}{\partial r_p}) \tag{7.11}$$

The time and length of the reactor are simply related by

$$\frac{dZ}{dt} = u_p \tag{7.12}$$

The boundary condition for the partial differential equation is given by a heat balance at the gas solids interface.

$$\left.\frac{\partial v}{\partial r_p}\right|_{r_p=R_p} = \frac{h_c}{K_s} (T - v_s) \tag{7.13}$$

The initial condition is

$$v(o,r_p) = \phi(r_p) \tag{7.14}$$

By symmetry,

$$\left.\frac{\partial v}{\partial r_p}\right|_{r_p = 0} = 0 \tag{7.15}$$

The system thus consists of a set of nonlinear first order ordinary differential equations and a second order parabolic partial differential equation. The solution is difficult because of the coupling boundary condition (7.13) for the partial differential equation. The method of solution found successful decouples the two sets by replacing the coupling boundary condition for the solids surface temperature by an explicit function of time. The gas and solids equations are now solved separately and the energy changes in both phases calculated. The function is adjusted until the overall energy balance checks.

It is assumed that for a small increment of time, the solids surface temperature changes linearly, e.g.,

$$v_s = v_s^{(0)} + b\,\tau$$

where the superscript "0" signifies the beginning of the time increment and b is some constant to be determined by matching the enthalpy changes in the gas and solid phases.

A semianalytical technique is used to obtain a solution of the partial differential equation$^{(71)}$. In this method, the space derivatives are discretised and a set of difference differential equations are obtained. The derivation of the partial differential equation and the discretisation are shown in Appendix F. The discretised equation can be written in the form

$$\underline{G}\,\frac{d\underline{y}}{d\theta} = \underline{B}\,\underline{y} + \underline{S}(\theta) \qquad (7.16)$$

Certain properties of matrix algebra are now used to obtain a solution of the matrix differential equation in a closed form as

$$\underline{y}(\theta,r_p) = \underline{G}^{-1/2}\underline{Q}\underline{E}(\theta)\underline{Q}^T\underline{G}^{1/2}\,[\underline{y}^{(0)} + \int_0^\theta \underline{G}^{-1/2}\underline{Q}\underline{E}^{-1}(\sigma)\underline{Q}^T\underline{G}^{-1/2}\underline{S}(\sigma)d\sigma] \qquad (7.17)$$

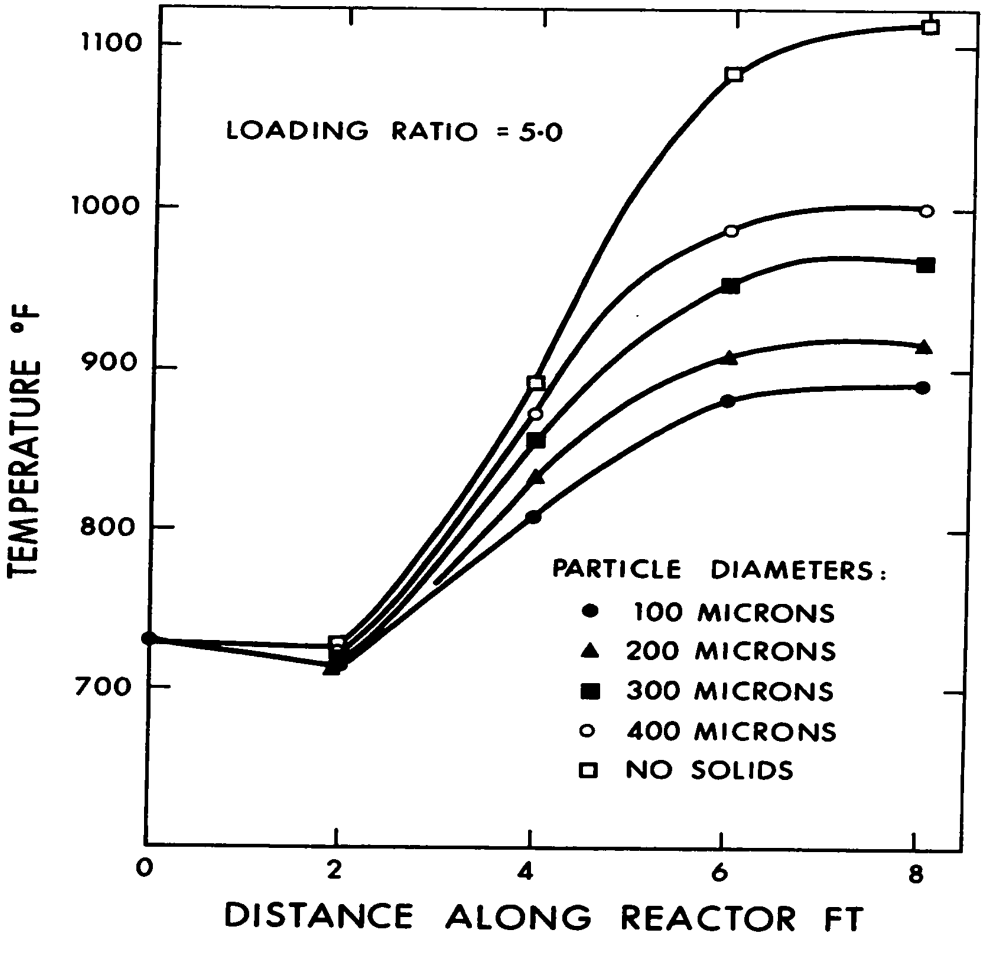


FIGURE 7.1 GAS TEMPERATURE-EFFECT OF PARTICLE SIZE

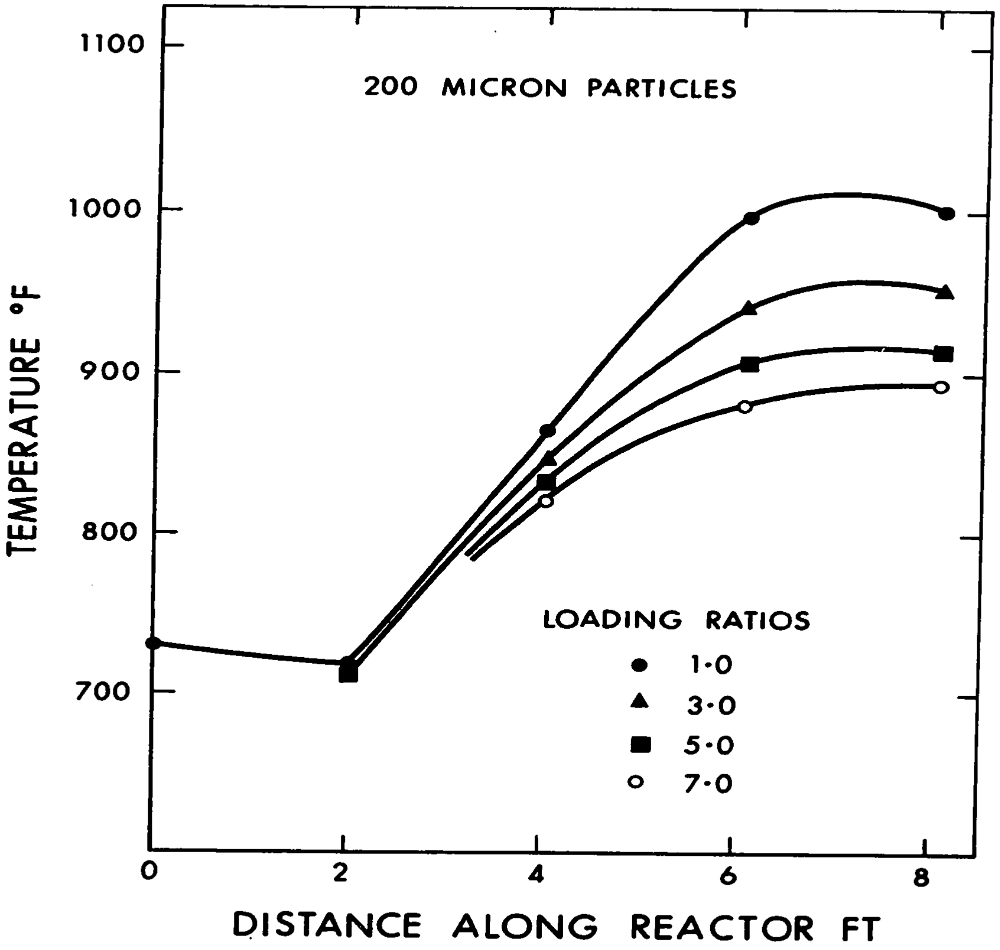


FIGURE 7.2 GAS TEMPERATURE-EFFECT OF LOADING RATIO

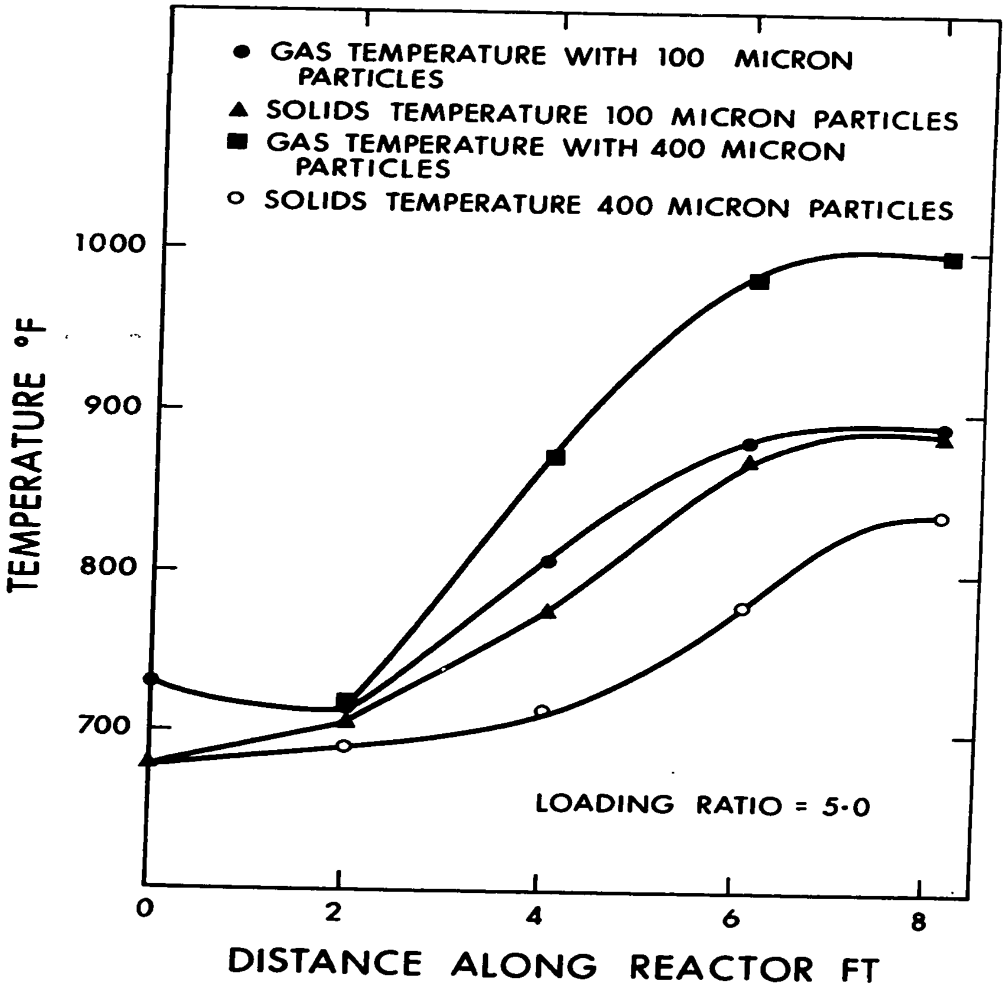


FIGURE 7.3 TEMPERATURES OF GAS AND SOLIDS PHASES

To solve the gas phase equations, a time average value of the solids surface temperature can be used.

$$v_s = v_s^{(0)} + \frac{b\,\tau}{2}$$

Runge Kutta method of integration has been generally used to solve the gas phase equations. The modification of Merson discussed by Lapidus$^{(72)}$ to control the step size was found to decrease the integration time, as compared to the straight forward use of the Runge Kutta method with a fixed step size.

Figures 7.1 and 7.2 show the effect of particle diameters and the loading ratios. Both these variables have significant effect on the temperature distribution in the reactor and a desired profile can likely be achieved in the reactor. Figure 7.3 shows the temperatures of the gas and solids for 100 micron and 400 micron diameter particles. It is seen that for 100 micron particles, the solids temperature follows closely the gas temperature.

Numerical investigations were carried out for a range of 50 micron to 800 micron diameter particles. In this range, it was found that the solids temperatures do not significantly vary along the radius and so the solids can be considered to reach uniform temperature across the cross section. This simplifies the transported bed model very significantly, reducing it to a system of first order nonlinear ordinary differential equations. This in turn makes the parameter estimation problem of a transported bed reactor much easier.

In cases where a larger range of particle diameters are used, the numerical method presented in this section can be readily used to solve the problem and to check the validity of the simplification offered by the use of uniform particle temperature.

7.3 Experimental Investigations

7.3.1 Results from Transported Bed Reactor

A number of runs were conducted in the transported bed reactor in order to obtain the temperature profiles, overall conversions and the product selectivity, and to compare with those of the homogeneous reactor. The experimental runs are summarized in Table 7.1 and the temperature profiles are presented in Table D.2 in the appendix.

The solids flow rates were measured by weighing the total amount of solids collected for each run. The capacity of the feeder was limited by the dimension of the rectangular slots cut into the rotor in the solids feeder. The feeder becomes unstable if operated beyond 70-80 rpm. The reactor, therefore, could not be operated at loading ratios higher than 3.0 to 5.0. For such loading ratios, the maximum temperature of the reactor was reduced by about 150°F. The temperature profile was flattened and so also the conversions. Figures 7.4 and 7.5 show the temperature profiles and conversions for some of the runs.

7.3.2 Comparison with Homogeneous Reactor

Figures 7.6 to 7.11 show the comparison for two runs, run 65 for the homogeneous reactor and run 77 for the transported bed reactor, both conducted at the same hydrocarbon to oxygen ratio. There is a difference of 140°F in the maximum temperature obtained, and the final yield of the oxygenated products increases from 0.30 mole/mole *n*-butane reacted for the homogeneous run to 0.50 mole/mole *n*-butane reacted for the TBR. Much of this increase results from an increased amount of methanol whose amount rises from 0.17 mole/mole *n*-butane reacted to 0.30 mole on the same basis. There is some increase in the amount of the olefins and a

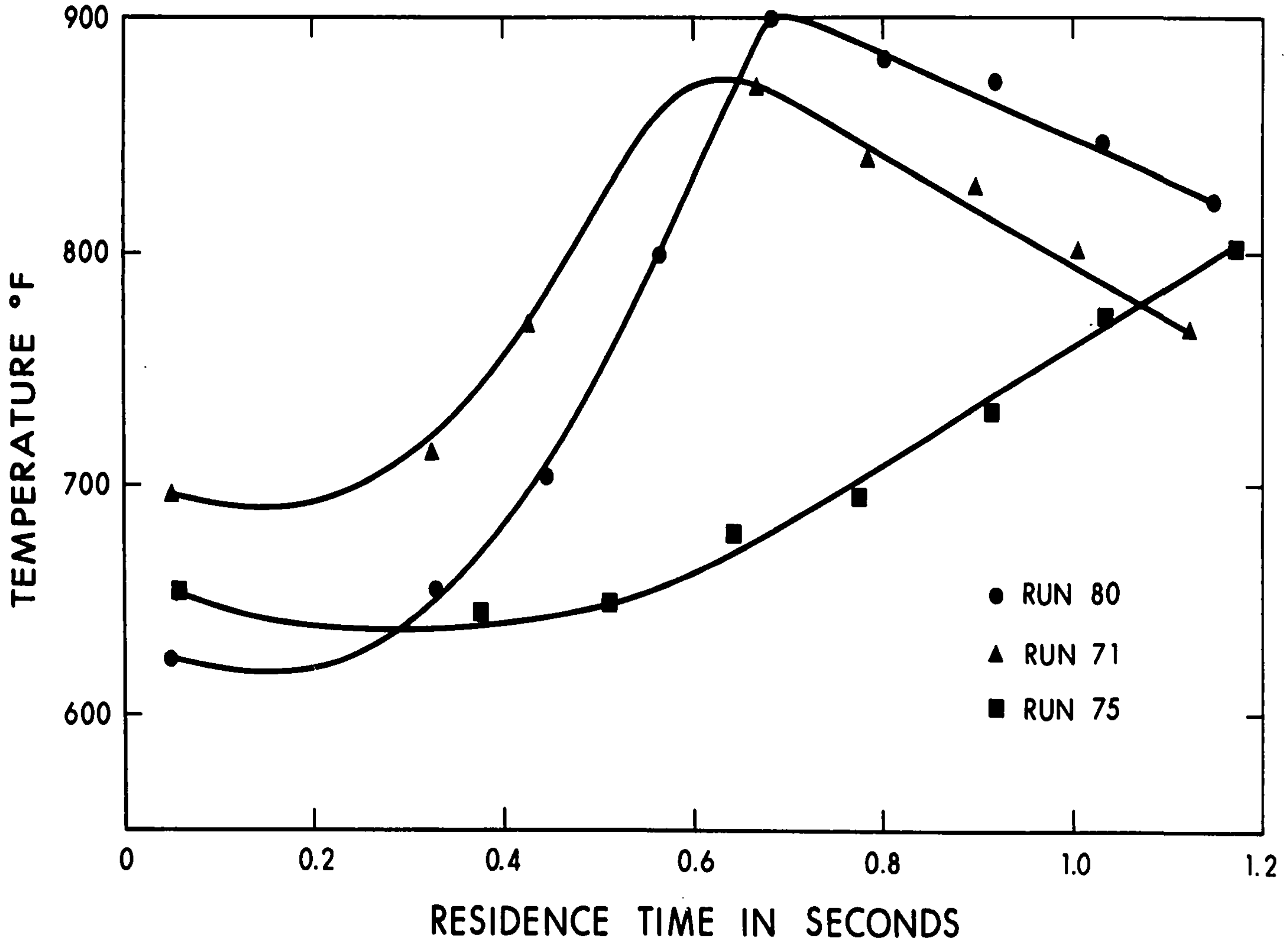


FIGURE 7.4 GAS TEMPERATURE PROFILES IN TRANSPORTED BED REACTOR

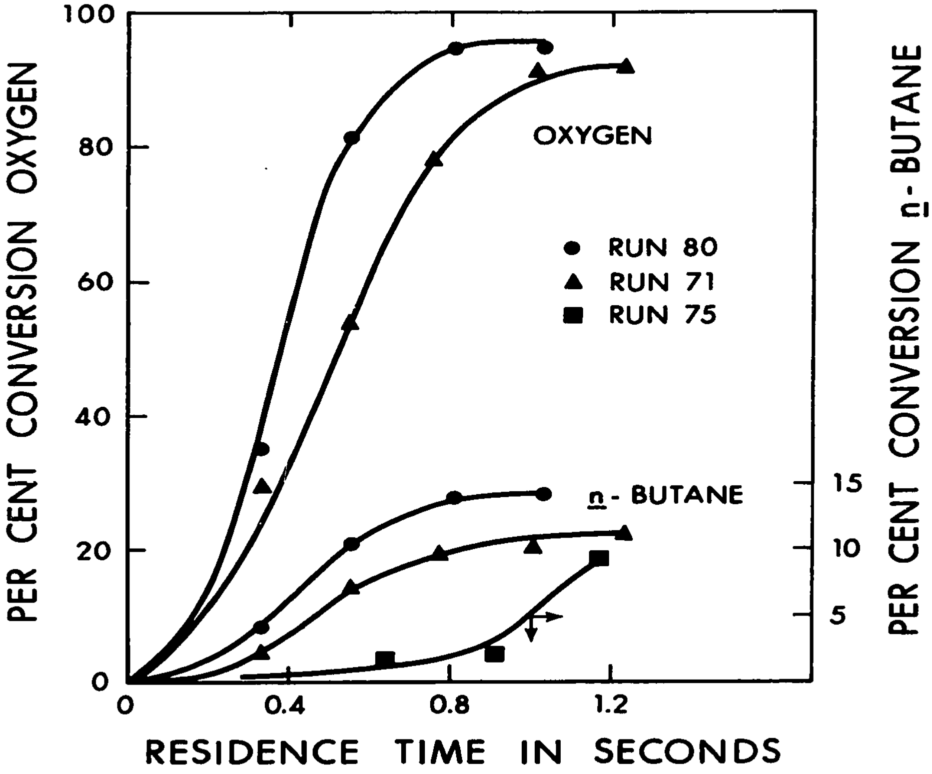


FIGURE 7.5 OVERALL CONVERSIONS IN TRANSPORTED BED REACTOR

TABLE 7.1

EXPERIMENTAL RUN DETAILS

Run Number	Inlet Temperature °F	Pressure psia	_n_-butane: oxygen	Loading Ratio	Residence Time second	Inlet Reynolds Number
71	698	51.40	10.7	3.0	1.25	6402
73	678	53.72	9.4	3.0	1.38	6015
75	655	51.35	8.4	5.0	1.44	5492
77	650	53.50	7.4	4.0	1.27	6245
80	625	53.50	6.8	3.2	1.26	6412

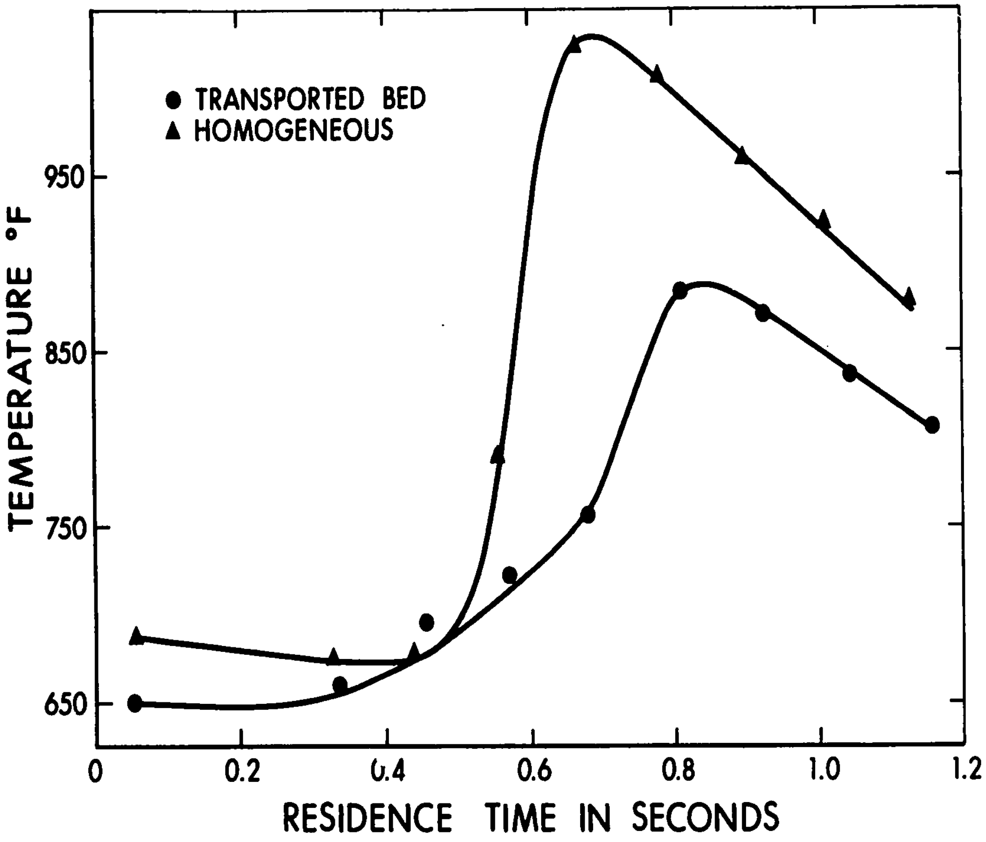


FIGURE 7.6 TEMPERATURE PROFILES: COMPARISON BETWEEN HOMOGENEOUS AND TRANSPORTED BED RUNS

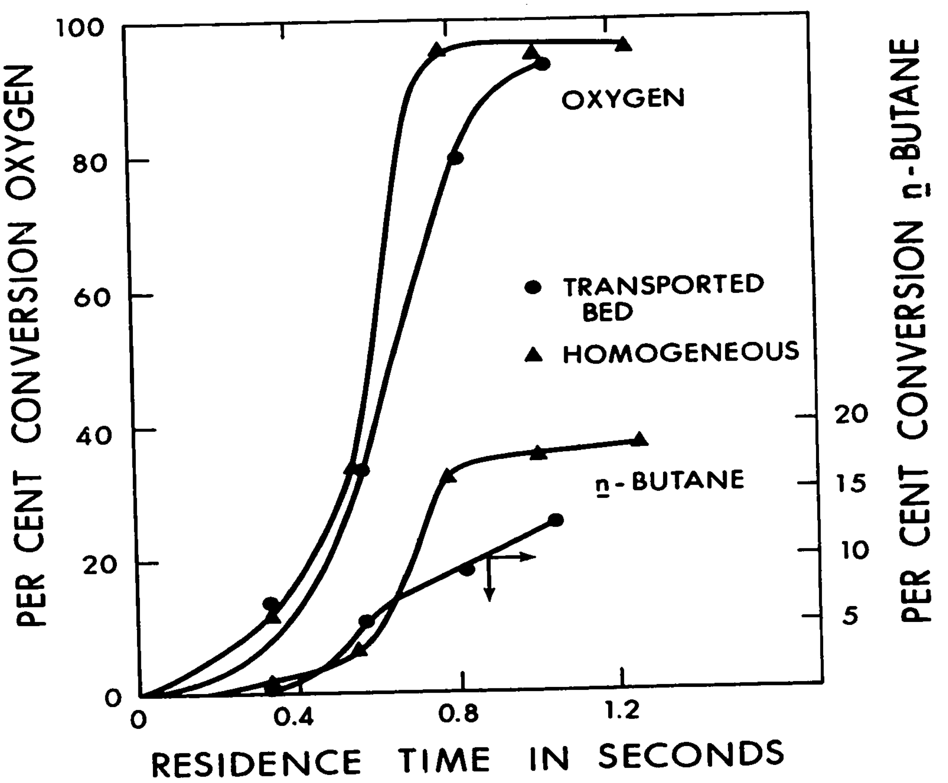


FIGURE 7.7 OVERALL CONVERSIONS - COMPARISON BETWEEN HOMOGENEOUS AND TRANSPORTED BED RUNS

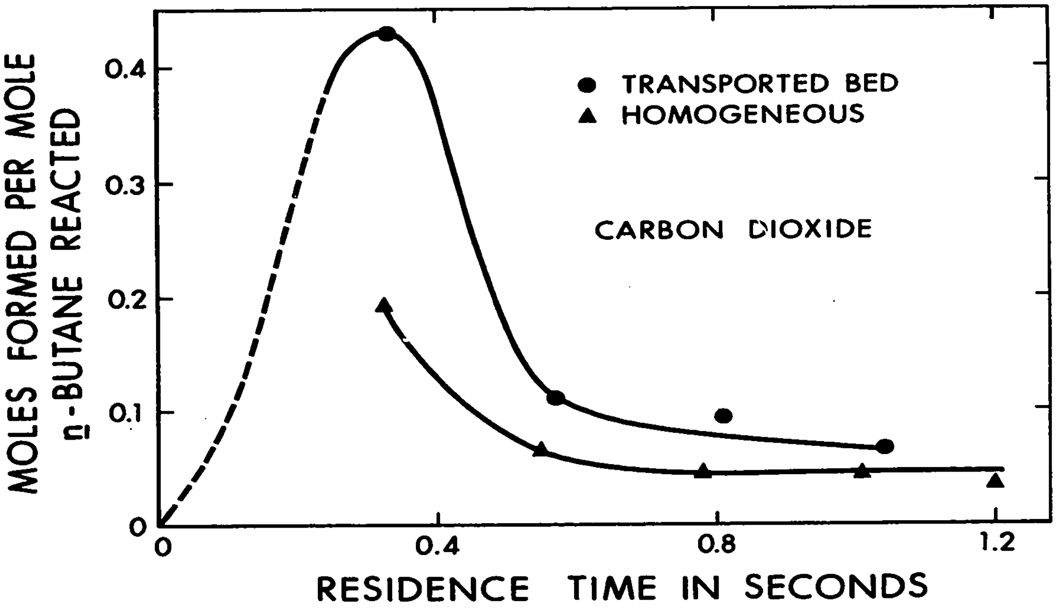


FIGURE 7.8 SELECTIVITY - COMPARISON BETWEEN HOMOGENEOUS AND TRANSPORTED BED RUNS

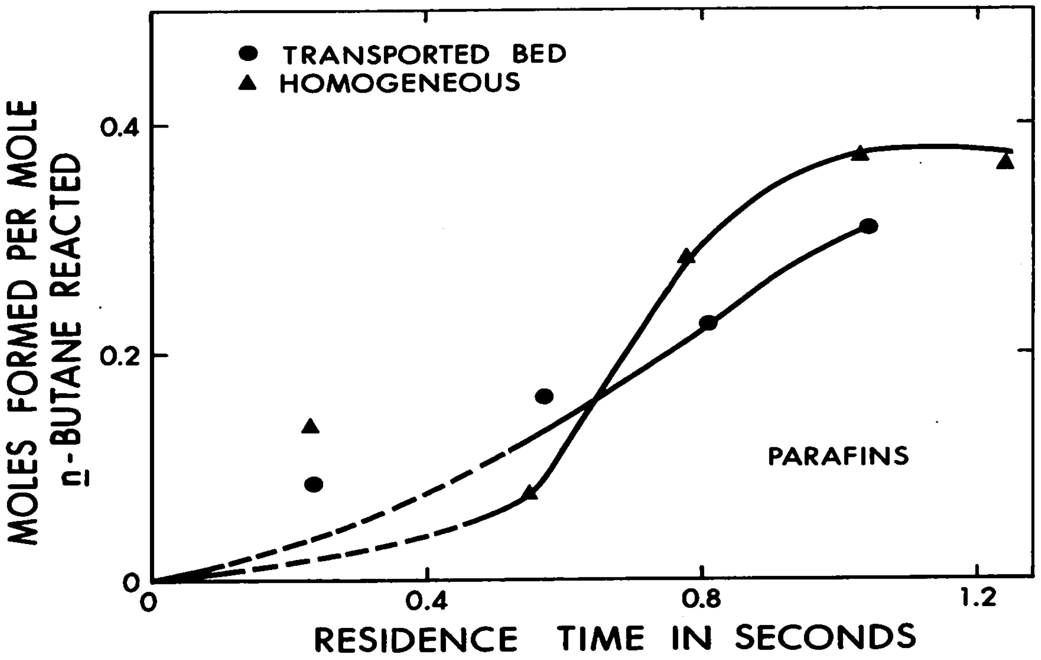


FIGURE 7.9 SELECTIVITY - COMPARISON BETWEEN HOMOGENEOUS AND TRANSPORTED BED RUNS

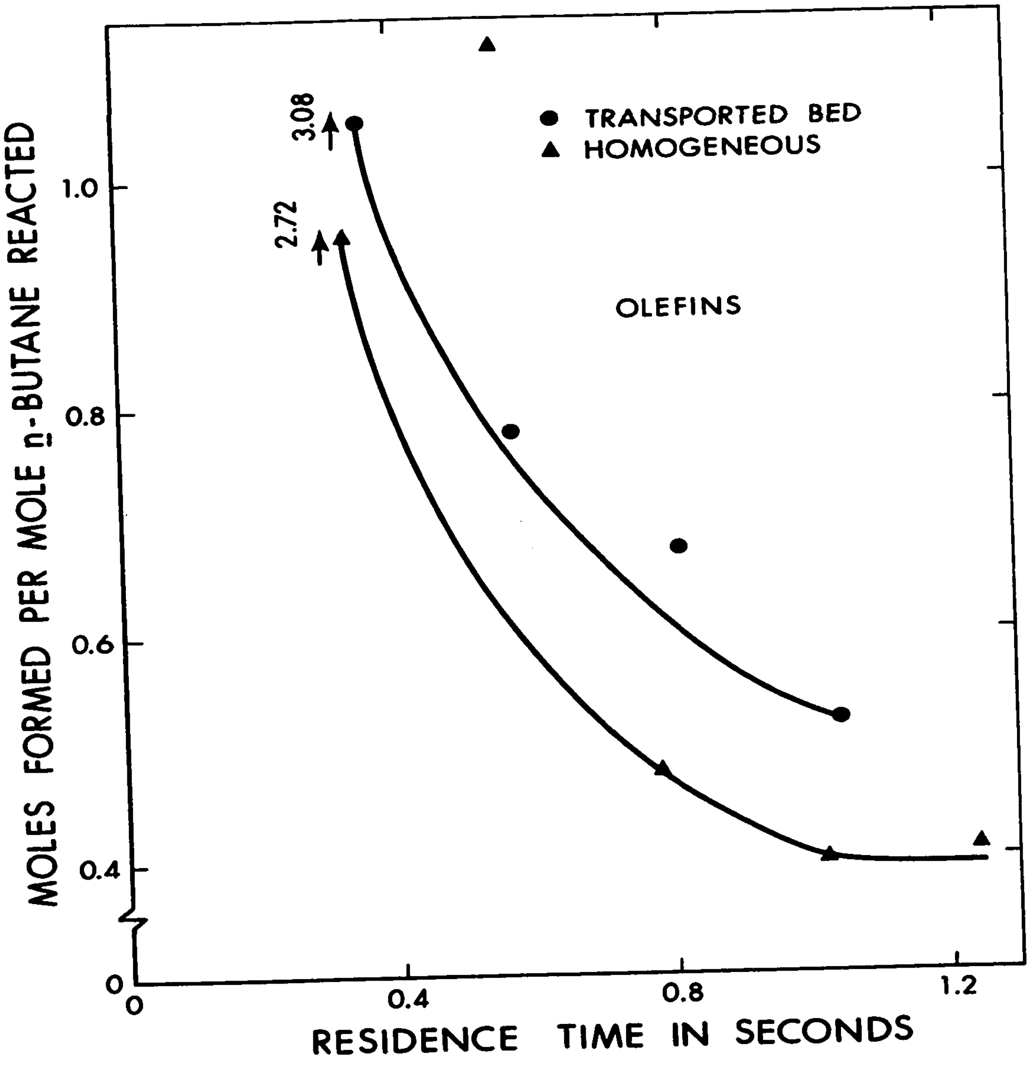


FIGURE 7.10 SELECTIVITY - COMPARISON BETWEEN HOMOGENEOUS AND TRANSPORTED BED RUNS

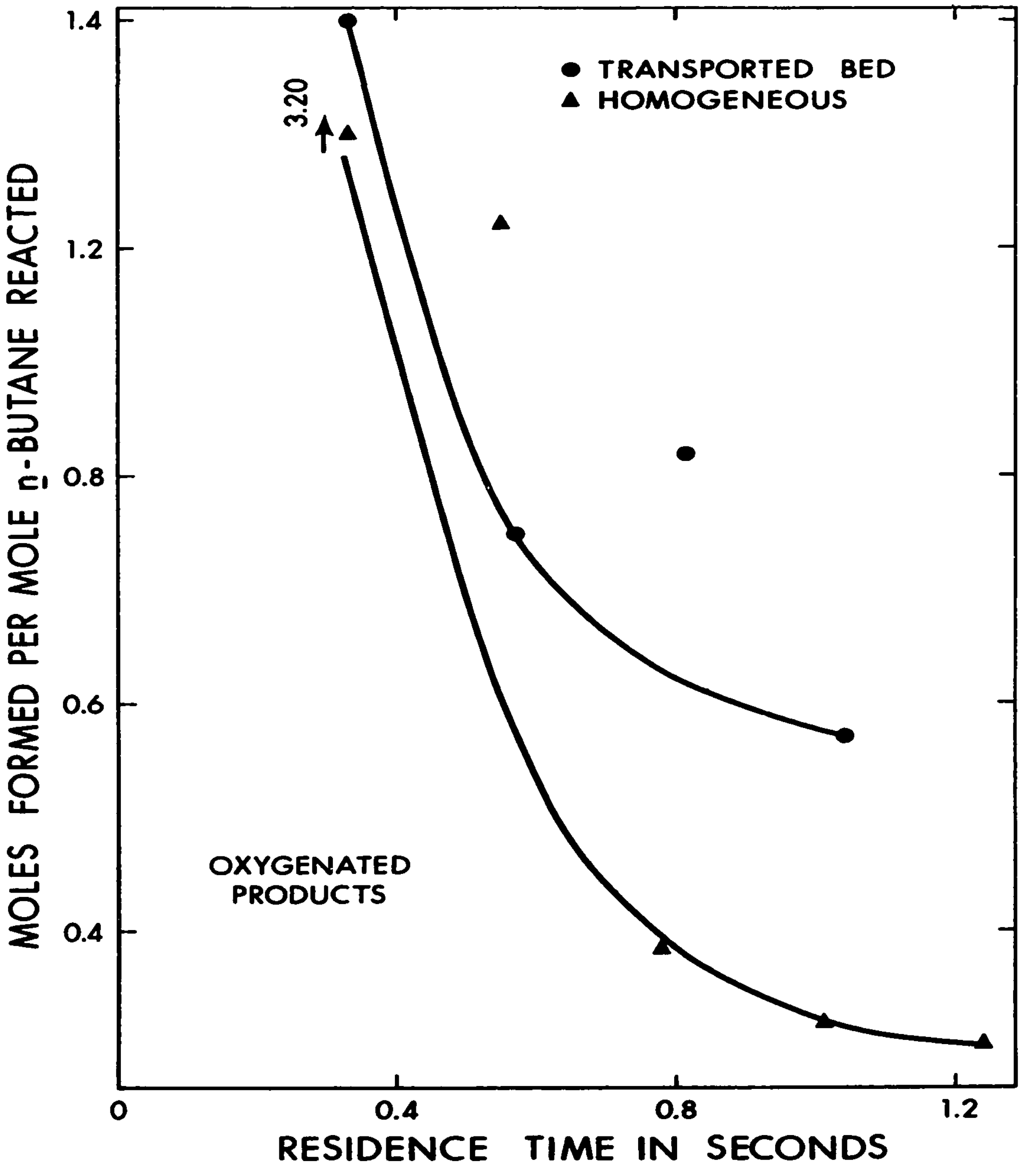


FIGURE 7.11 SELECTIVITY - COMPARISON BETWEEN HOMOGENEOUS AND TRANSPORTED BED RUNS

decrease in the amount of paraffins obtained in the reactor. The time of rapid reaction increases from about 0.15 seconds to about 0.25 seconds, thus making the reaction more tractable.

7.3.3 Surface Effects

The use of solid particles in the transported bed reactor introduces additional surface. The voidage in the reactor is over 99 per cent and the reaction takes place essentially in an empty tube. However, the reaction in many cases have been reported to be surface sensitive and it was desirable to obtain the effects of surface, if any, in the transported bed reactor.

For this purpose, a new selectivity is defined and is called the relative yield. This is expressed as moles of a component formed per mole n-butenes formed in the reaction. The butenes were used as a basis because they are generally believed to be formed from homogeneous reactions. Figures 7.12 to 7.16 show the relative yields for runs 65 and 77. There is generally a greater yield of oxygenated products and lesser yield of cracking products in the case of a transported bed reactor. The product distribution is not altered in the presence of solid particles to any significant extent which would suggest that the surface has affected the relative yield. In the range of the present experimental program, it is therefore concluded that the reaction in the TBR took place by the same mechanism as in the case of the homogeneous reactor. The solid particles in the TBR simply acted as heat sink and did not in any way change the homogeneous character of the reaction. It is also argued that since the additional surface did not reveal any effect of the surface, the formation of all the products in the partial oxidation of n-butane takes place homogeneously. The present study therefore did not

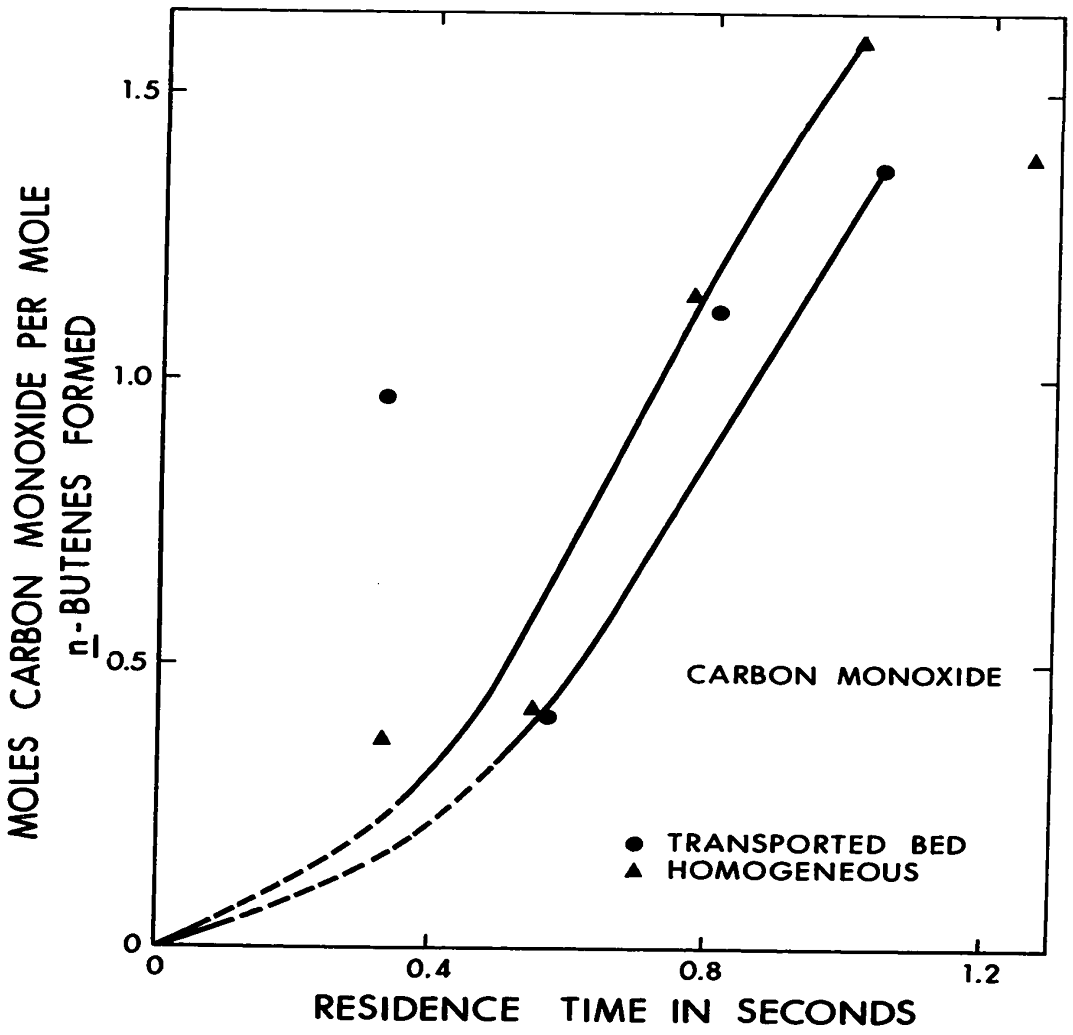


FIGURE 7.12 RELATIVE YIELD - EFFECT OF SURFACE

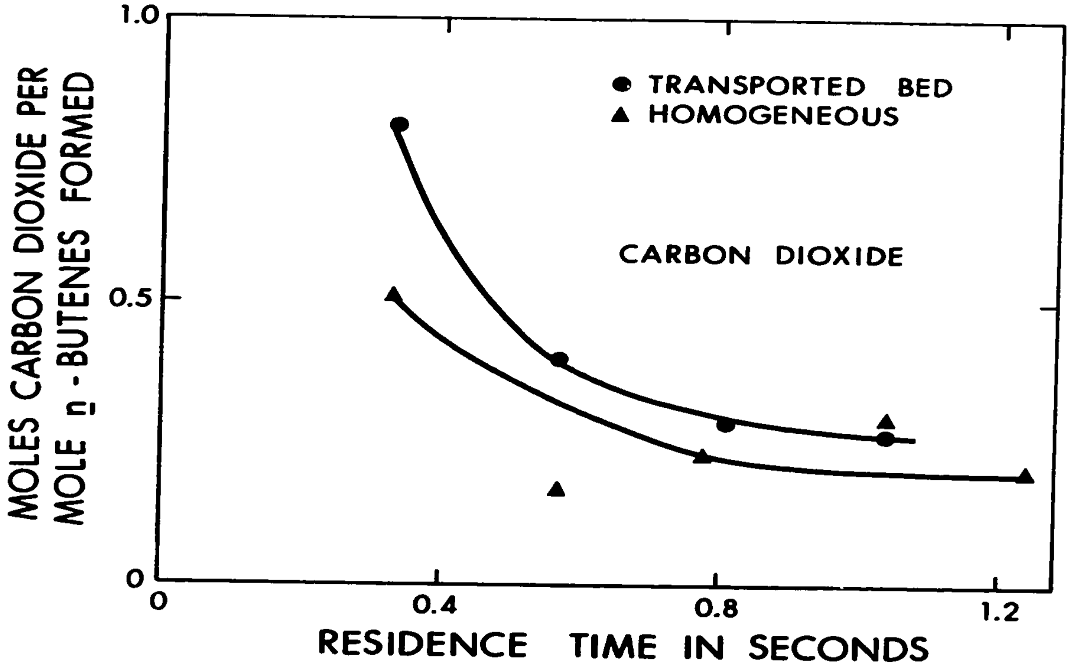


FIGURE 7.13 RELATIVE YIELD - EFFECT OF SURFACE

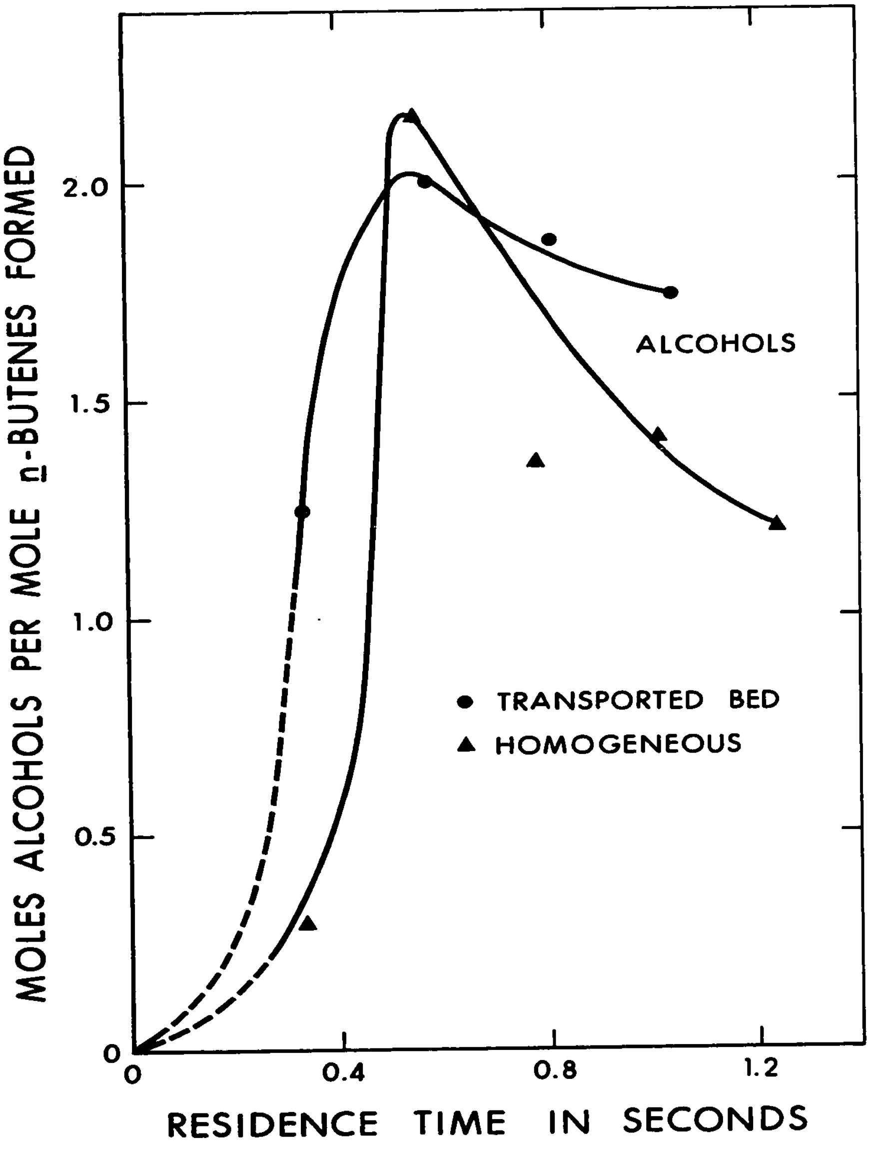


FIGURE 7.14 RELATIVE YIELD - EFFECT OF SURFACE

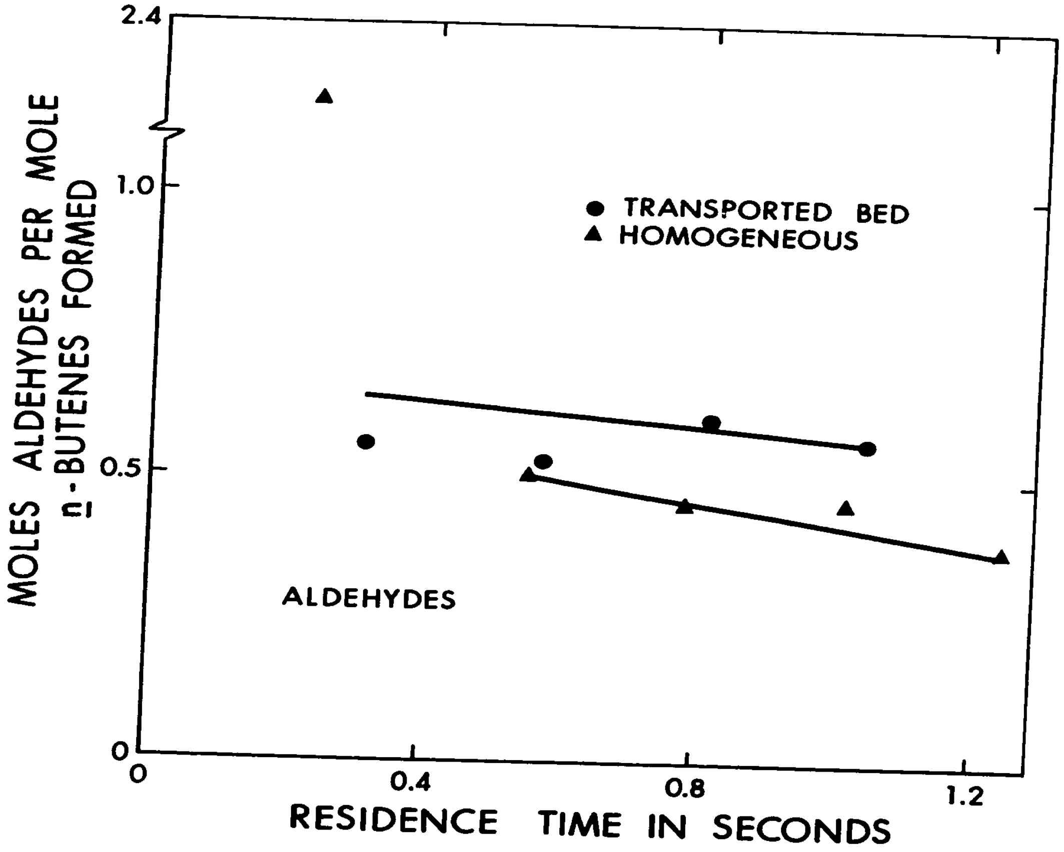


FIGURE 7.15 RELATIVE YIELD - EFFECT OF SURFACE

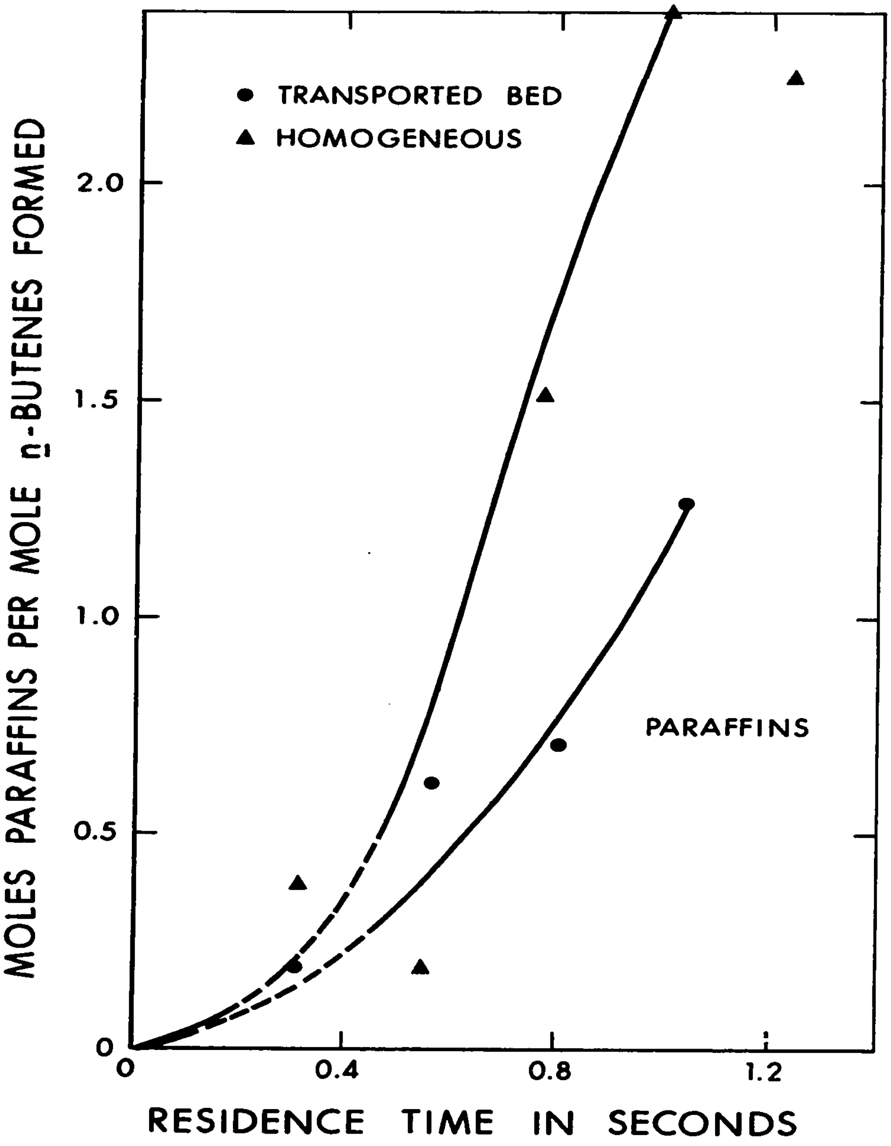


FIGURE 7.16 RELATIVE YIELD - EFFECT OF SURFACE

support the observations by Knox(18) who suggested that the oxygenated products are formed by heterogeneous reactions at the surface. It is possible that in the slow combustion region investigated by Knox at subatmospheric pressure, the homogeneous propagation steps were slow enough to permit radical diffusion to the wall and reaction thereon to become important product forming steps.

7.4 Application of Homogeneous Kinetic Models

In the previous section it was hypothesized that the mechanisms of the reaction of hydrocarbon with oxygen remains unaltered by the presence of solid particles in the transported bed reactor. In that case, the same kinetic models as postulated for the homogeneous reactor could, therefore, be applied. It was found, however, that the models always predicted lower temperature profiles for the gas. This was attributed to the uncertainties in the thermal model for the system represented by equations 7.3 and 7.4 in section 7.2. The heat transfer coefficients calculated from equations in the literature(69) may be in considerable error. Preliminary runs with the model showed that it was not sensitive to a change in the heat transfer coefficient from gas to wall, but was quite sensitive to the heat transfer coefficient between the solids and the gas, h_c. With a correction factor of 0.8, the predicted temperature profiles matched well with the experimental profiles. In other words, the heat transfer coefficients determine the level of the temperature profiles, while the kinetic coefficients determine their shape.

The results after this modification are presented in Table 6.7. It is found that mechanism II predicts the overall conversions for *n*-butane and oxygen and the temperature profiles quite well. This is in

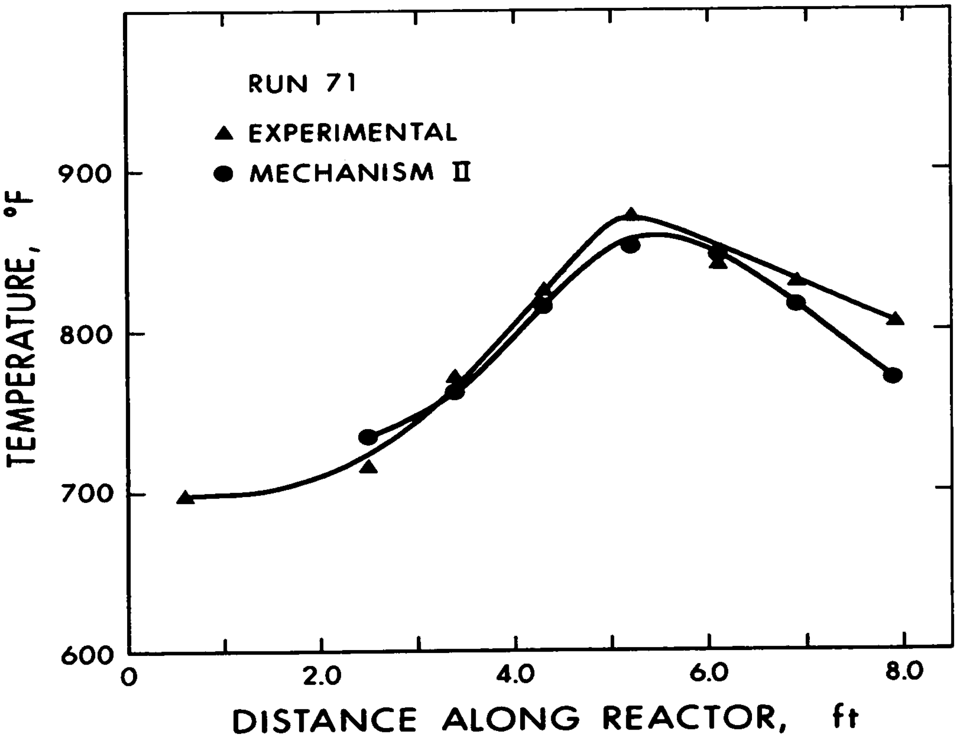


FIGURE 7.17 EXPERIMENTAL AND PREDICTED TEMPERATURE PROFILES

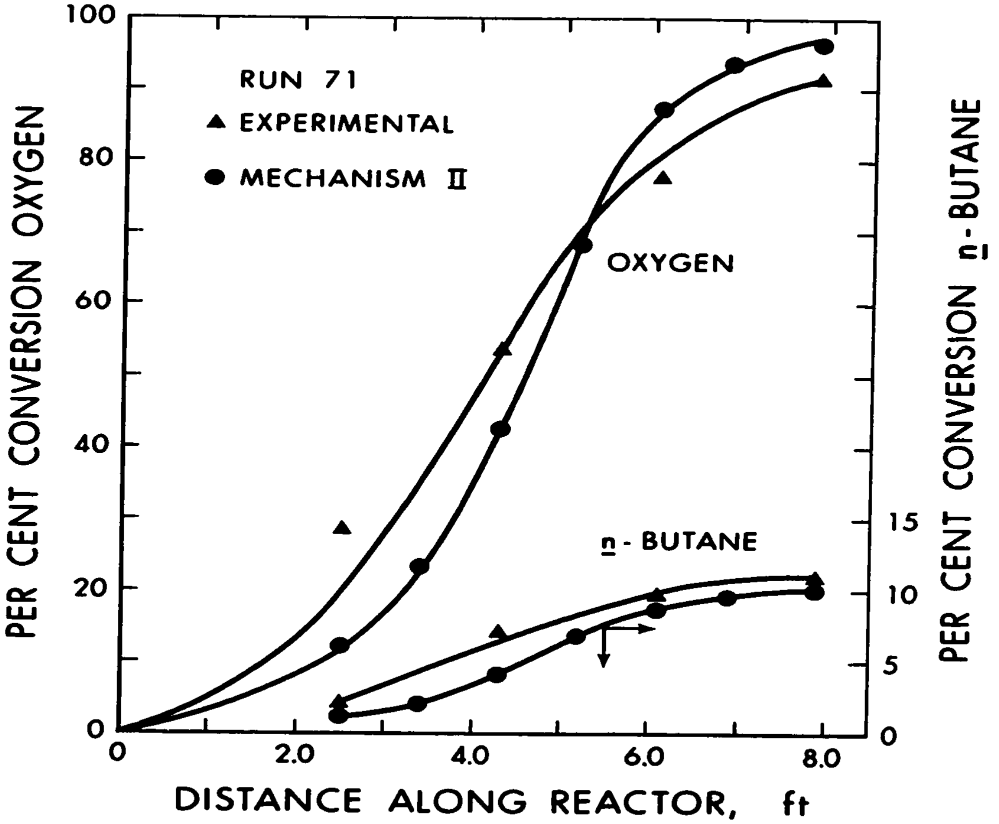


FIGURE 7.18 EXPERIMENTAL AND PREDICTED CONVERSIONS

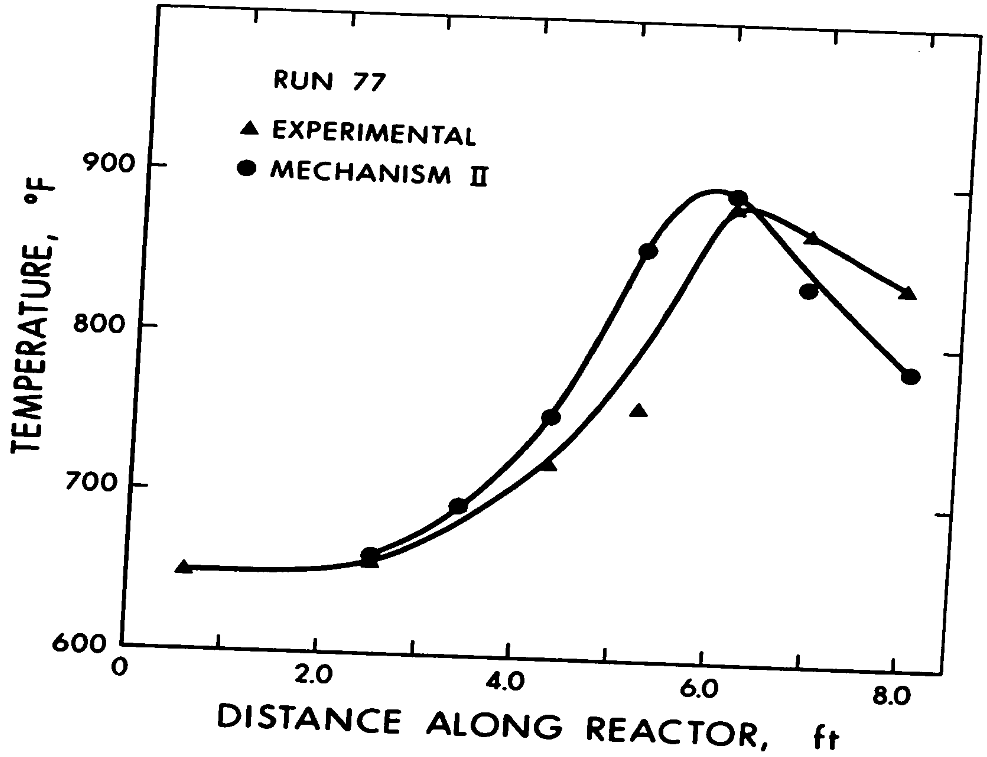


FIGURE 7.19 EXPERIMENTAL AND PREDICTED TEMPERATURE PROFILES

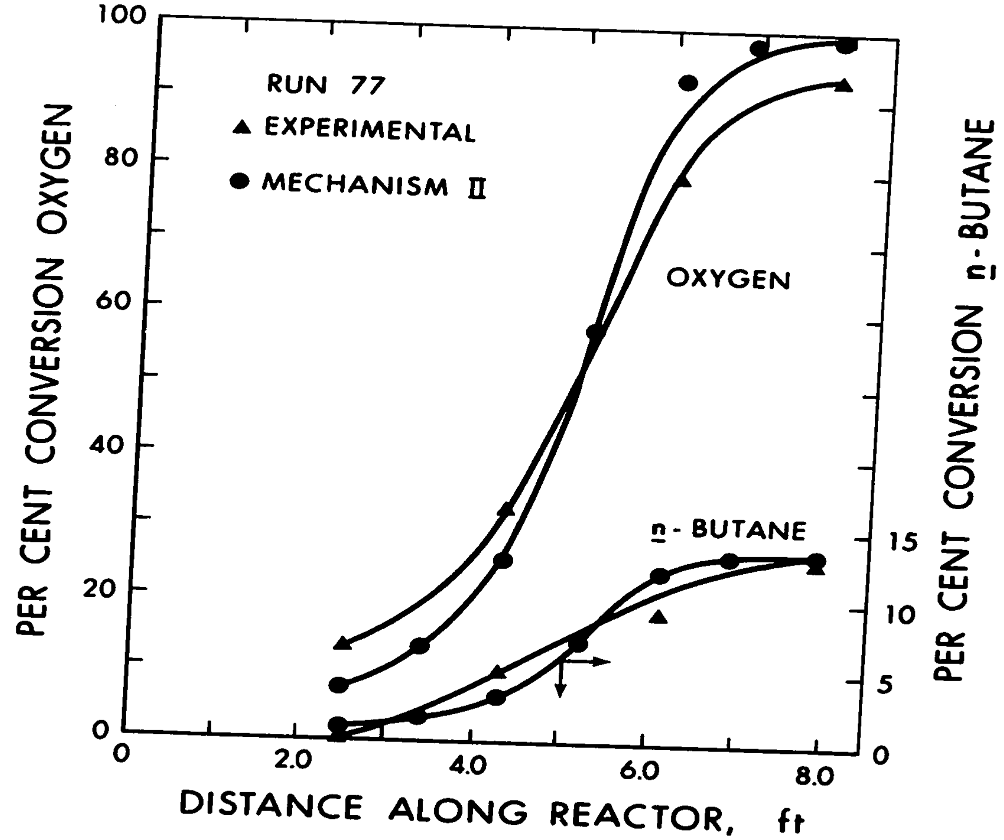


FIGURE 7.20 EXPERIMENTAL AND PREDICTED CONVERSIONS

accord with the results for the homogeneous runs in which case also model II is better. Figures 7.17 to 7.20 show the predicted and experimental temperature profiles and conversions for runs 71 and 77.

7.5 Summary

The solution of the mathematical model for the transported bed reactor revealed that solid particles of the range of up to 800 microns in diameter attain almost uniform temperature across the radius.

A transported bed reactor was used in the present investigation for the partial oxidation of _n_-butane. A lower temperature rise and an improved selectivity were obtained as compared to the homogeneous reactor. No effect of surface was observed on the product distribution for the range of loading ratios considered. The kinetic schemes for the homogeneous reactor was used and mechanism II predicted the overall conversions and temperature profiles fairly well. A correction factor was used for the gas solids heat transfer coefficient to match the experimental temperature profiles.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

A transported bed reactor system was developed which allowed a method of temperature control by the use of solid particles without having any undesirable effect on the overall reaction and product distribution. The maximum temperature rise was cut down by 150F° and the selectivity to oxygenated products was almost doubled compared to a similar run in a homogeneous reactor. The length of time for the rapid reaction was increased and the monitoring of the progress of the reaction was made easier.

The overall behaviour of the reaction was studied in the homogeneous reactor. Higher hydrocarbon to oxygen ratio was found to be beneficial to the formation of the oxygenated compounds. The inlet temperature did not influence the overall course of the reaction.

The homogeneous runs allowed the development of an aggregate model for the reaction. Two kinetic schemes were postulated for the homogeneous reaction and their parameters estimated. The models were tested against independent runs. The same kinetic models with modifications of the thermal parameters could successfully predict the overall conversions and temperature profiles for the transported bed reactor.

8.2 Recommendations

The use of the transported bed reactor provides an effective means of controlling the temperature rise without inhibition of the reaction. It may now be possible to use artificial initiator and start the reaction at a low temperature and continue the reaction at the lower temperature level. This method is likely to improve the selectivity very significantly.

The range of investigation in the transported bed system can be increased by increasing the capacity of the solids feeder. This should be done by cutting deeper slots in the existing rotor. The solids heating system was inadequate, as the solids could not be heated beyond 650°F. A more compact solids heating unit should be built to replace the existing one.

NOMENCLATURE

A	Pre-exponential factor, normalized
A'	Pre-exponential factor, hr^{-1} or $ft^3/lb\text{-mole}/hr$
A_r	Cross-sectional area, ft^2
A_s	Solids surface area, ft^2/ft
A_w	Surface area of reactor wall, ft^2/ft
C	Specific heat of gas, Btu/lb/°F
C_A	Concentration of *n*-Butane, $lb\text{-mole}/ft^3$
C_B	Concentration of Oxygen, $lb\text{-mole}/ft^3$
C_C	Concentration of intermediate, $lb\text{-mole}/ft^3$
C_D	Drag coefficient, dimensionless
C_p	Specific heat of solid particles, Btu/lb/°F
D_r	Diameter of reactor, ft
d_p	Diameter of solid particles, ft
E	Activation energy, Btu/lb-mole
f	Friction factor, dimensionless
G_g	Gas flow rate, lb-mole/hr
G_o	Inlet gas flow rate, lb-mole/hr
g_c	Gravitational constant, $lb_m ft/lb_f sec^2$
h_c	Gas to solids heat transfer coefficient, $Btu/hr/ft^2/°F$
h_w	Gas to wall heat transfer coefficient, $Btu/hr/ft^2/°F$
ΔH	Heat of reaction, Btu/lb-mole
K	Reaction rate constant, hr^{-1} or $ft^3/lb\text{-mole}/hr$
K_s	Thermal conductivity of solids, $Btu/hr/ft^2\text{-}ft/°R$
m	Gas flow rate, lb/hr
m_p	Solids to gas loading ratio, dimensionless

NOMENCLATURE (continued)

m_p^*	Initial solids to gas loading ratio, dimensionless
N	Number of solid particles/ft reactor, ft^{-1}
P	Pressure, lb/in^2
Q_g	Gas phase heat transfer, Btu
Q_s	Solids phase heat transfer, Btu
R	Universal gas constant, ft-lb/lb/°F or Btu/lb-mole/°R
R_p	Particle Radius, ft
r	Reaction rate, $lb\text{-}mole/hr/ft^3$
r_p	Particle radius, ft
T	Gas temperature, °R
T_p	Mean particle temperature, °R
t	Time, hour
u	Velocity of gas, ft/sec
u_p	Velocity of particle, ft/sec
V	Temperature of solid particles, °R
V_s	Surface temperature of solid particles, °R
v	Specific volume of gas, ft^3/lb
w_p	Solids flow rate, lb/hr
x_A	Conversion of Butane, dimensionless
x_B	Conversion of Oxygen, dimensionless
x_C	Accumulation of intermediate, dimensionless
y_o	Inlet molar composition, fraction
Z	Distance along reactor, ft
α	Thermal diffusivity, ft^2/hr
ε	Void fraction, dimensionless

NOMENCLATURE (continued)

ρ	Gas density, lb/ft^3
ρ_p	Solids density, lb/ft^3
ρ_{ps}	Particulate phase density, lb/ft^3
τ	Time increment, hour
θ	Reduced time, dimensionless
μ	Viscosity of gas, lb/ft/hr

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APPENDIX A

EQUIPMENT DETAILS

The thermocouple and sample point locations are given in Table A.1. The temperature that the thermocouple measures is indicated by "G" if the thermocouple is in the gas stream, and by "W" if it is in the reactor wall. The location of the preheater and reactor control thermocouple is also indicated.

The properties of the solid particles and some of the equipment details are also presented.

TABLE A.1

Location of Thermocouples and Sample Points

Thermocouple Number	Temperature Measured	Location: Inches From Mixing Point	Sample Number
1	G	30.4	1
2	W	30.4	
3	G	41.1	
4	G	51.8	2
5	W	51.8	
6	G	62.5	
7	G	73.2	3
8	W	73.2	
9	G	83.9	
10	G	94.6	4
11	W	94.6	
12	G	105.3	
13	G	116.0	5
14	W	116.0	
15	Preheater		
16	Reactor	51.8	

Solid Particles

Material: Norton Crystalon (Silicon Carbide grain)

Physical Properties:

Size: 150 mesh

Crystal form: hexagonal system - hemihedral class

Melting temperature: dissociates at about 4170°F

True specific gravity: 3.20

Thermal conductivity at 800°F: 175 Btu/hr/ft^2-in/°F

Specific heat at 750°F: 0.277 Btu/lb/°F

Chemical Properties:

General resistance to chemical action: high

Resistance to air oxidation: up to 2900°F

Typical Analysis:

Component	weight per cent
SiC	97.6
SiO_2 (free)	0.8
Si (free)	0.5
C (free)	0.6
Fe	0.2
Al	0.2
Ca	0.05
Mg	0.05
	100.00

Electric Heaters

Solids Preheater:

Heating elements: Nikrothal 80 wire B & S 11

No. of elements: 14 elements in series

Inside diameter of heaters: 9.0 inches

Outside diameter: 11.5 inches

Maximum rating: 2.78 kw

Maximum current: 40 amps

Maximum voltage: 208 volts

Arrangement: 3 heaters in parallel

Gas Preheater:

Kanthal heaters

Heating length: 19.7 inches

Inside diameter: 5.0 inches

Outside diameter: 6.5 inches

Maximum rating: 5.873 kw

Maximum current: 55 amps

Maximum voltage: 107 volts

Arrangement: 2 heaters in series

Reactor heater:

Kanthal heaters

Heating length: 19.70 inches

Inside diameter: 1.57 inches

Outside diameter: 2.58 inches

Maximum rating: 1350 watts

Maximum voltage: 30 volts

Maximum current: 45 amps

Arrangement: 5 heaters in series

Control Systems

Pressure Controller:

Foxboro Model 58 P4 pneumatic controller

Pressure transmitter:

Foxboro M144 pressure transmitter

Control Valves:

Foxboro Type V4 needle valve, body size 1/2 inch, needle size 1/8 inch (c_v = 0.07) for air flow.

For n-butane flow, the same except needle size 0.024 inch (c_v = 0.0052).

For back pressure valve at reactor exit, needle size 3/16 inch (c_v = 0.28).

Flow Controllers:

For air and n-butane flow controls, Foxboro Model 58 Universal Pneumatic Controller.

Temperature Controllers:

For gas and solid preheaters, Foxboro Model 62 Universal Electronic Controller. The final control element is a Vectrol VS6002 Silicontrol Gate Drive. For reactor, Honeywell controller model R7161J. Model R4205A SCR power module provides solid state switching to the heaters.

APPENDIX B

RETENTION TIMES FOR THE COMPONENTS SEPARATED BY GAS CHROMATOGRAPHY

SAMPLE CHROMATOGRAMS

The retention times for all the components separated on each column are given in Tables B.1 and B.2. The relative response factors and the correction factors are also included. Correction factors are not reported for the Molecular Sieve-Charcoal column, because this column is operated at constant temperature. The component numbers, given for all components, are used in Appendix E for the compounds reported in the analysis and product distributions.

Sample chromatograms are shown in order to indicate the degree of separation obtained in each column. The components separated and the attenuation for each peak are given on the chromatograms.

TABLE B.1

Retention Times for Components Separated On Porapak S Column

Component Number	Component	Retention Time mins	Relative Response Factor	Correction Factor
1	Hydrogen	1.5	0.0085	1.0
2	Oxygen	1.5	0.40	1.0
3	Nitrogen	1.5	0.42	1.0
4	Carbon monoxide	1.8	0.42	1.0
5	Methane	2.5	0.36	1.0
6	Ethylene	5.5	0.48	1.0
7	Ethane	7.0	0.51	1.0
8	Propylene	16.4	0.63	1.04
9	Propane	17.0	0.65	1.04
10	*i*-Butane	22.9	0.82	1.03
11	1-Butene	21.6	0.81	1.04
12	2-Butene	23.6	0.86	1.03
13	*n*-Butane	24.2	0.85	1.05
14	2-Methyl Butane	37.2	1.05	1.05
15	*n*-Pentane	38.0	1.05	1.06
16	Carbon dioxide	3.5	0.42	1.0
17	Water	14.5	0.31	1.02
18	Formaldehyde	15.4	0.58	1.03
19	Methanol	21.0	0.58	1.05
20	Acetaldehyde	26.2	0.69	1.05
21	Ethanol	31.5	0.74	1.06
22	Ethylene Oxide	32.7	0.68	1.06
23	Acetone	33.7	0.86	1.05
24	Propionaldehyde	34.5	0.80	1.04
25	Propylene Oxide	35.3	0.80	1.05
26	*n*-Propanol	38.7	0.83	1.10
27	Butyraldehyde	39.3	0.92	1.07
28	Methyl Ethyl Ketone	46.0	0.98	1.08

TABLE B.1 (continued)

29	Sec-Butanol	50.5	0.97	1.10
30	Diethyl Ketone	53.0	1.10	1.10

TABLE B.2

Retention Times for Components Separated On Charcoal-Molecular Sieve Column

Component Number	Component	Retention Time mins	Relative Response Factor
1	Hydrogen	2.5	0.0085
2	Oxygen	4.5	0.40
3	Nitrogen	5.0	0.42
4	Carbon Monoxide	7.5	0.42
5	Methane	13.0	0.36

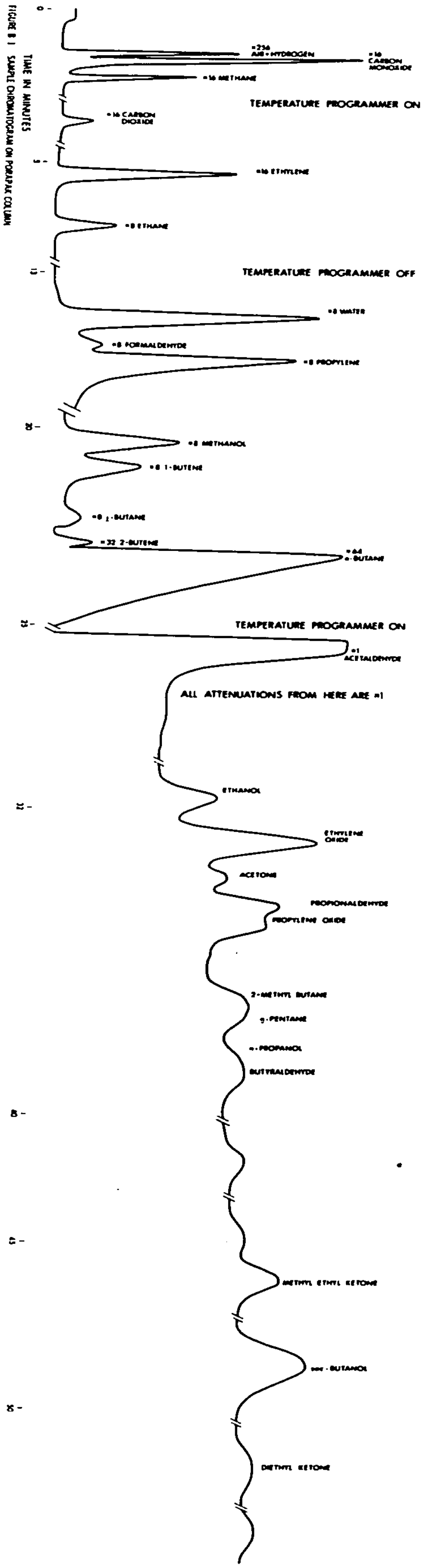

FIGURE B 1 SAMPLE CHROMATOGRAM ON PORAPAK COLUMN

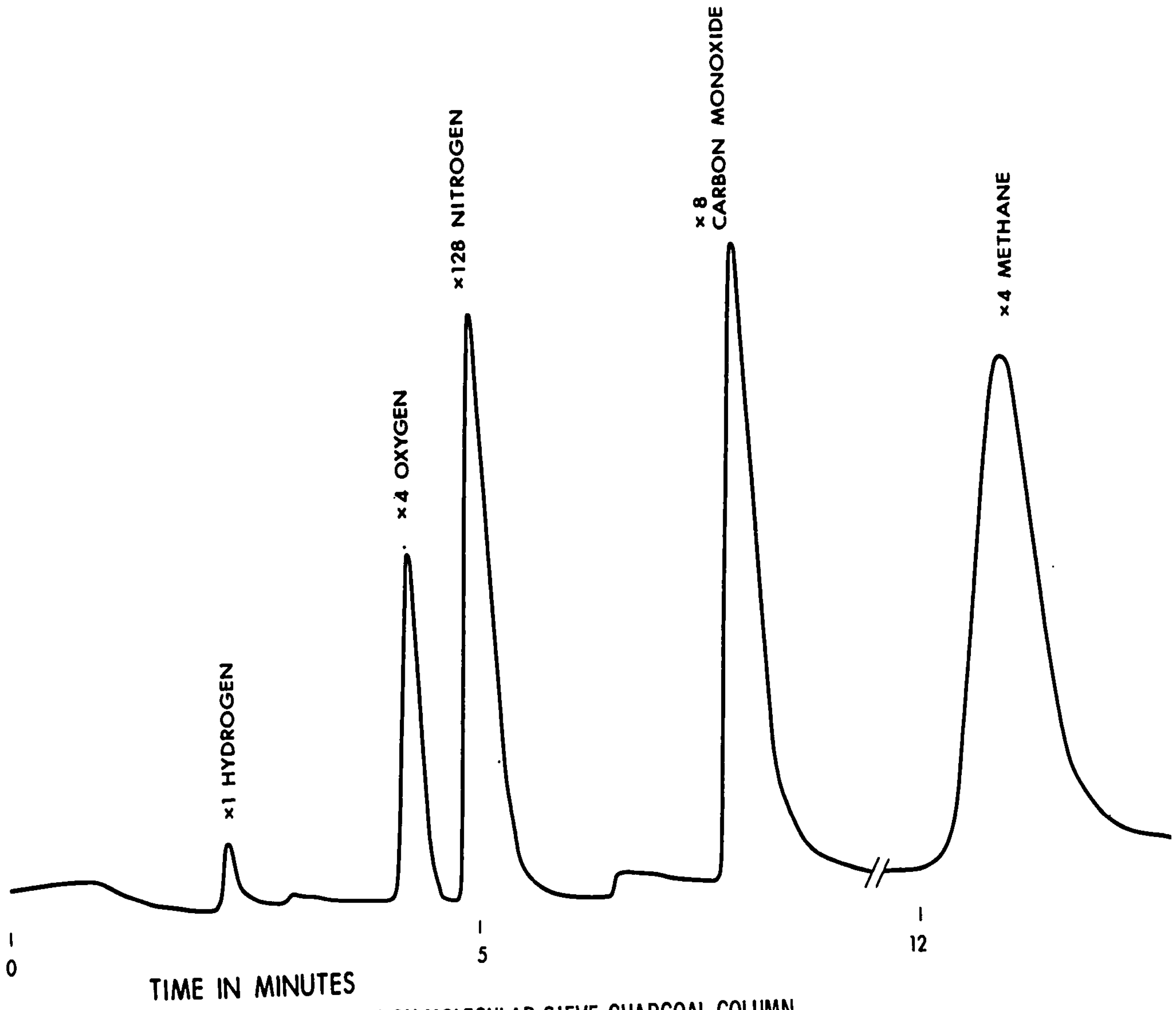

FIGURE B.2 SAMPLE CHROMATOGRAM ON MOLECULAR SIEVE-CHARCOAL COLUMN

APPENDIX C

CALIBRATION OF INSTRUMENTS

Calibration of Instruments

The D/P cells and the pressure transmitter were calibrated following standard procedures and the results are presented in Tables C.1, C.2 and C.3. The flow rates are plotted in Figures C.1 and C.2.

The D/P cell for n-butane was calibrated with water and then converted to n-butane by the formula given by Foxboro as:

$$\text{Equivalent water flow (gpm)} = V\, G_b \sqrt{\frac{1}{G_f}}$$

where V = flow of liquid n-butane in gpm at 60°F,
G_b = specific gravity of n-butane at 60°F,
G_f = specific gravity of n-butane at the flowing temperature.

Introduction of the proper values in the equation resulted in

$$n\text{-}C_4 \text{ (lb/hr)} = 0.755 \times \text{water (lb/hr)}$$

The calibration of the pressure transmitter is given in Table C.3. The calibration was found to be essentially exact over the entire range.

TABLE C.1

D/P Cell Calibration For Air

Orifice Diameter	0.0595 inches
D/P Cell Range	100 inches of water
Air Temperature	72°F
Atmospheric Pressure	698 mm Mercury

Controller Chart Reading per cent	Air Rate cu ft/min	Air Rate NTP cu ft/min	Air Rate lb/hr
35	0.51	0.434	2.10
65	0.705	0.598	2.90
82	0.776	0.66	3.20
49	0.606	0.515	2.50
55	0.655	0.556	2.70
40	0.564	0.478	2.32

TABLE C.2

D/P Cell Calibration for n-Butane

Orifice Diameter	0.02 inches
D/P Cell Range	250 inches of water
Water Temperature	70°F

Controller Chart Reading per cent	Water Rate lb/hr	n-Butane Rate lb/hr
41.4	10.52	7.95
59.4	12.68	9.56
21.9	7.39	5.57
79.6	14.8	11.18
90.4	15.81	11.95
34.2	9.36	7.07
51.9	11.82	8.94
41.4	10.38	7.84

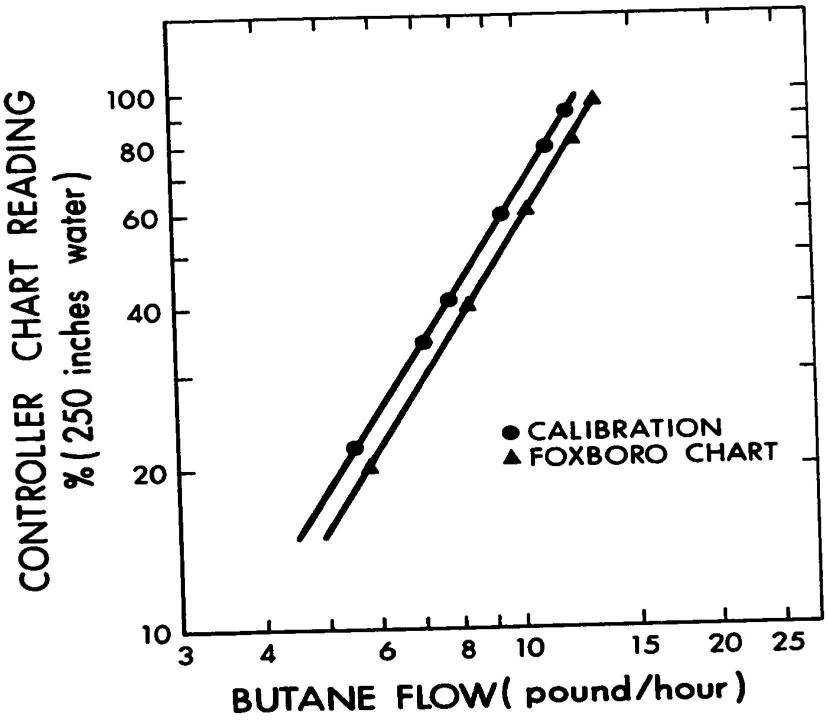

FIGURE C.1 CALIBRATION OF D/P CELL

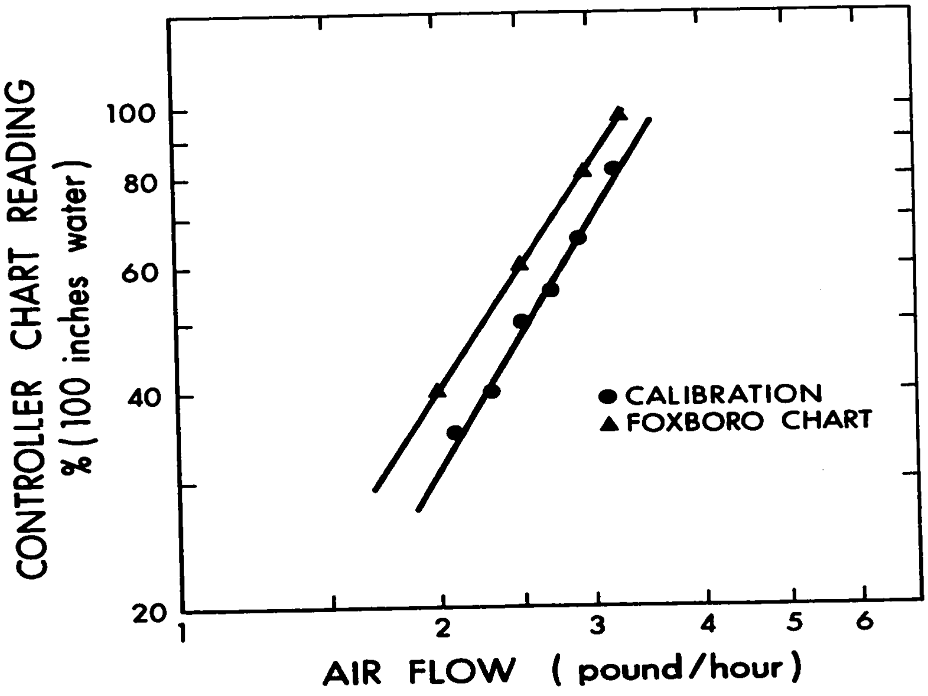

FIGURE C.2 CALIBRATION OF D/P CELL

TABLE C.3

Pressure Transmitter Calibration

Actual Pressure psig	Transmitter Pressure psig	Recorder Chart Reading per cent
20	20.0	10.0
40	40.0	20.0
50	50.0	25.0
70	70.0	35.0
80	80.0	40.0
100	100.0	50.0
150	150.0	75.0
200	200.0	100.0

APPENDIX D

EXPERIMENTAL TEMPERATURE PROFILES

The experimental temperatures for the homogeneous runs are presented in Table D.1 and those for the transported bed runs in Table D.2. All readings are the actual thermocouple recorded millivolts converted to degrees Fahrenheit. The errors due to conduction and radiation between the thermocouple and the reactor wall have been estimated to be about 12°F(1). Since the fluctuation in the temperature readings especially in the region of rapid reaction rate is much higher, no attempt has been made to correct for the radiation and conduction errors.

TABLE D.1

Experimental Temperature Profiles

Run Number	60	61	62	63	64	65	66	67	68
Thermocouple Number	Temperature °F								
15	685	695	695	702	692	687	708	684	684
1	658	666	672	684	666	672	705	667	672
2 W	660	667	672	689	670	690	727	698	692
3	655	678	676	696	670	679	830	705	685
4	700	737	705	820	714	790	1006	850	910
5 W	672	715	726	875	714	724	942	930	828
6	800	895	913	1041	825	1025	1040	1053	1004
7	915	950	970	1032	1025	1008	1002	971	915
8 W	804	810	852	912	870	889	896	820	828
9	870	910	932	997	1006	963	970	943	920
10	835	860	886	937	927	924	930	864	870
11 W	747	750	795	840	774	807	840	725	798
12	810	817	860	900	804	883	895	823	852
13	768	777	816	835	798	828	850	755	795
14 W	570	558	613	630		570	630		590

TABLE D.2

Experimental Temperature Profiles

Run Number	71	73	75	77	80
Thermocouple Number	Temperature °F				
15	698	678	655	650	625
1	715	650	648	660	655
2 w	740	668	665	692	750
3	770	660	650	695	705
4		690	680	722	800
5 w	805	730	715	830	850
6	872	740	692	758	900
7	842	800	735	885	885
8 w	740	770	710	755	805
9	830	830	775	870	875
10	805	860	805	838	850
11 w	670	730	695	660	740
12	770	840	810	810	825
13	730	800	785	755	795

APPENDIX E

EXPERIMENTAL RESULTS: HOMOGENEOUS AND TRANSPORTED BED REACTORS

Reactor entrance conditions are calculated from the n-butane and air flow rates, the reactor pressure and the temperature at the entrance to the reactor. The calculation procedure is indicated below:

$$\text{Mole \% Oxygen} = 21 \left(\frac{\text{Air Flow Rate in lb moles/hr}}{\text{Total Flow Rate in lb moles/hr}}\right)$$

$$\text{Mole \% Nitrogen} = 79 \left(\frac{\text{Air Flow Rate in lb moles/hr}}{\text{Total Flow Rate in lb moles/hr}}\right)$$

$$\text{Mole \% } \underline{\text{n}}\text{-Butane} = 100\left(\frac{\underline{\text{n}}\text{-Butane Flow Rate in lb moles/hr}}{\text{Total Flow Rate in lb moles/hr}}\right)$$

$$\text{Ratio of } \frac{\text{Oxygen}}{\text{Nitrogen}} = \frac{\text{Mole \% Oxygen}}{\text{Mole \% Nitrogen}}$$

$$\text{Ratio of } \frac{\underline{\text{n}}\text{-Butane}}{\text{Nitrogen}} = \frac{\text{Mole \% } \underline{\text{n}}\text{-Butane}}{\text{Mole \% Nitrogen}}$$

$$\text{Density of the entering gas, } \rho_o = \frac{mP}{RT}$$

$$\text{Entrance Velocity, } u_o = \frac{w}{3600\ A\ \rho_o}$$

$$\text{Residence Time, } \tau_o = \frac{L}{u_o}$$

$$\text{Reynolds Number, } Re = \frac{D\ u_o\ \rho_o}{\mu}$$

A = cross-sectional area of the reactor, ft^2

D = inside diameter of reactor, ft

L = overall length of reactor, ft

m = average molecular weight of feed stream

P = reactor pressure, psia

R = gas constant

T = temperature of gases at entrance, °R

u_o = velocity of gases at entrance, ft/sec

w = weight rate of flow of gases, lb/hr

ρ_o = density of gases at entrance, lb/ft^3

τ = residence time of the gases based on the entrance conditions, sec

μ = viscosity of gases at entrance, lb/ft.hr

For each product sample, the areas are converted to mole per cent by the use of the relative response factors and the correction factors. The procedure is as follows:

Calculate $\frac{\text{Component Area}}{\text{Relative Response Factor}}$ for each component or group of components on the Porapak S column and the Molecular Sieve-Charcoal column and find the total

$$TOT_{PR} = \sum \frac{\text{Component Area}}{\text{Relative Response Factor}}$$

$$TOT_{MS-C} = \sum \frac{\text{Component Area}}{\text{Relative Response Factor}}$$

Subscripts PR and MS-C refer to Porapak S and Molecular Sieve-Charcoal columns, respectively.

$$\%\ \text{Component}_{PR} = \frac{100}{TOT_{PR}} \times \frac{\text{Component Area}}{\text{Relative Response Factor}}$$

$$\%\ \text{Component}_{MS-C} = \frac{100}{TOT_{MS-C}} \times \frac{\text{Component Area}}{\text{Relative Response Factor}}$$

The first peak in Porapak column contains hydrogen, oxygen and nitrogen. The first three peaks in Molecular Sieve-Charcoal column contain these components. Hence, their compositions can be obtained by multiplying the air peak by the proportions in which these components are present in Molecular Sieve-Charcoal column.

The percentage composition is converted to moles per mole nitrogen as follows:

$$\frac{\text{Moles Component}}{\text{Moles Nitrogen}} = \frac{\text{Mole \% Component}}{\text{Mole \% Nitrogen}}$$

A number of other calculations can now be made. The carbon, hydrogen and oxygen balances are made as follows:

$$\text{\% Carbon Balance} = \frac{100 \text{x} \sum \frac{\text{Moles Component}}{\text{Moles Nitrogen}} \text{ x } \begin{array}{c}\text{No. of Carbon Atoms}\\ \text{in Component}\end{array}}{4 \text{ x } \frac{\text{Moles } \underline{\text{n}}\text{-Butane}}{\text{Moles Nitrogen}} \text{ in the feed}}$$

$$\text{\% Hydrogen Balance} = \frac{100 \text{x} \sum \frac{\text{Moles Component}}{\text{Moles Nitrogen}} \text{ x } \begin{array}{c}\text{No. of Hydrogen Atoms}\\ \text{in Component}\end{array}}{10 \text{ x } \sum \frac{\text{Moles n-Butane}}{\text{Moles Nitrogen}} \text{ in the feed}}$$

$$\text{\% Oxygen Balance} = \frac{100 \text{x} \sum \frac{\text{Moles Component}}{\text{Moles Nitrogen}} \text{ x } \begin{array}{c}\text{No. of Oxygen Atoms}\\ \text{in Component}\end{array}}{2 \text{ x } \frac{\text{Moles Oxygen}}{\text{Moles Nitrogen}} \text{ in the feed}}$$

The per cent conversions of oxygen and n-butane can be found out.

$$\text{\% Oxygen Reacted} = 100 \left(\frac{\frac{\text{Moles Oxygen}}{\text{Moles Nitrogen}} \text{ in the feed} - \frac{\text{Moles Oxygen}}{\text{Moles Nitrogen}} \text{ in the Product}}{\frac{\text{Moles Oxygen}}{\text{Moles Nitrogen}} \text{ in the feed}} \right)$$

$$\text{\% } \underline{\text{n}}\text{-Butane Reacted} = 100 \left(\frac{\frac{\text{Moles } \underline{\text{n}}\text{-Butane}}{\text{Moles Nitrogen}} \text{ in the feed} - \frac{\text{Moles } \underline{\text{n}}\text{-Butane}}{\text{Moles Nitrogen}} \text{ in the Product}}{\frac{\text{Moles } \underline{\text{n}}\text{-Butane}}{\text{Moles Nitrogen}} \text{ in the feed}} \right)$$

The selectivities in terms of n-Butane and oxygen reacted are obtained as follows:

$$\frac{\text{Moles Component formed}}{\text{Mole Oxygen Reacted}} = \frac{\dfrac{\text{Moles Component formed}}{\text{Mole Nitrogen}}}{\dfrac{\text{Moles Oxygen Reacted}}{\text{Mole Nitrogen}}}$$

$$\frac{\text{Moles Component formed}}{\text{Mole } \underline{n}\text{-Butane Reacted}} = \frac{\dfrac{\text{Moles Component formed}}{\text{Mole Nitrogen}}}{\dfrac{\text{Moles } \underline{n}\text{-Butane Reacted}}{\text{Mole Nitrogen}}}$$

The per cent of carbon going to different types of products are calculated as follows:

% Conversion to Olefins =

$$100\left(\frac{\dfrac{\text{Moles Olefins in the Product}}{\text{Mole } \underline{n}\text{-Butane Reacted}}}{\dfrac{\text{Moles Total Reaction Products}}{\text{Mole } \underline{n}\text{-Butane Reacted}}}\right)$$

Similar conversions to other groups of components are obtained in the same way.

The relative yield of different products can also be obtained from the selectivity calculations.

$$\frac{\text{Moles Components formed}}{\text{Mole } \underline{n}\text{-Butenes formed}} = \frac{\dfrac{\text{Moles Component formed}}{\text{Mole } \underline{n}\text{-Butane Reacted}}}{\dfrac{\text{Moles } \underline{n}\text{-Butenes formed}}{\text{Mole } \underline{n}\text{-Butane Reacted}}}$$

The yield relative to other components can be obtained similarly.

The computer program that was used in making these calculations is presented, followed by the results of all the experiments performed in this study.

```
          C         CHROMATOGRAPH
C         CHROMATOGRAPH
C         THIS PROGRAM TAKES IN THE INITIAL CONDITIONS FOR
C         THE REACTOR AND THE PEAK AREAS FOR THE PRODUCTS
C         FORM THE GAS CHROMATOGRAPHIC ANALYSIS. IT THEN
C         CALCULATES THE PRODUCT COMPOSITIONS AND SELEC-
C         TIVITIES, CONVERSIONS AND MATERIAL BALANCES.
C
      INTEGER PAGE
      DIMENSION CAR(35),HYD(35),OXY(35),RSP(35),CRP(35)
     *,RSC(5),CRC(5)
      DIMENSION PRA(35),PRAM(35),PRAP(35),PRAPM(35),PCNT(35)
     *,PCNTM(35)
      DIMENSION CHA(5),CHAM(5),CHAP(5),CHAPM(5)
      DIMENSION CARB(35), RPN(35),HYDB(35),OXYB(35)
     *,RPTOX(35),RPTBT(35)
C         NT     NO. OF RUNS
C         NT     NO. OF RUNS
C         NP     NO. OF PEAKS IN PORAPAK COLUMN
C         NC     NO. OF PEAKS IN CHARCOAL-MOLECULAR SIEVE
C         COLUMN
C         JP     TOTAL NUMBER OF COMPONENTS PRESENT
C         NS     NUMBER OF SAMPLES
C         RPT    TOTAL MOLES PRODUCT PER MOLE BUTANE REACTED
C         OOXPR  MOLE OXYGENATED PRODUCT/MOLE OXYGEN REACTED
C         OXPR   MOLE CRACKING PRODUCT/MOLE OXYGEN REACTED
C         ORTN   TOTAL MOLE OXYGENATED PRODUCT/MOLE NITROGEN
C         CRTN   TOTAL MOLE CRACKING PRODUCT/MOLE NITROGEN
C         BOXPR  MOLE OXYGENATED PRODUCT/MOLE BUTANE REACTED
C         CRPR   MOLE CRACKING PRODUCT/MOLE BUTANE REACTED
C         RPT    TOTAL MOLES PRODUCT PER MOLE BUTANE REACTED
C
    1 FORMAT(3F10.0)
    2 FORMAT(2F10.0)
    4 FORMAT(4F10.0)
    5 FORMAT(5F10.0)
    6 FORMAT(2I4)
    9 FORMAT(9I4)
   29 FORMAT(1H0,44X,5H  E - ,I3///  21X,9HRUN NO = ,I3,2X
     *,12HSAMPLE NO
     2= ,I2)
   32 FORMAT(1H0,21X,58HPRD NO  MOL PERCENT  MOLS/MOL N2
     * MOLS/MOXY R  M
     2OLS/MBUT R)
   38 FORMAT(1H0,21X,6HTOTALS,3(2X,F11.6)//18X,16HCARBON
     * BALANCE,F12.6
     2,13H LB AT/MOLN2.,F9.2,8H PERCENT/18X,17HHYDROGEN
```

```
      C          CHROMATOGRAPH   ...(CONT'D)

     * BALANCE ,F11.6,1
     33H LB AT/MOLN2.,F9.2,8H PERCENT/18X,15HOXYGEN BALANCE
     *,F13.6,13H L
     4B AT/MOLN2., F9.2,8H PERCENT//18X,17HPERCENT O2 REACT
     *,F10.4,4X,17
     5HPERCENT C4 REACT ,F10.4)
   50 FORMAT(1HO,    44X,5H  E - ,I3/////21X,9HRUN NO = ,I3)
   51 FORMAT( 1HO,20X,27HREACTOR ENTRANCE CONDITIONS //)
   53 FORMAT(1HO,20X,6HAIR = ,F6.2,6H LB/HR,10X,9HBUTANE =
     *,F6.2,6H LB/H
     2R,//21X,14HTEMPERATURE = ,F8.2,7H DEG F ,//21X
     *,11HPRESSURE = ,F6.2
     3,9H LB/SQ IN,//21X,9HOXYGEN = ,F6.4,12H NITROGEN =
     *,F7.4,10H BUTAN
     4E = ,F7.4,1X,9H MOL PCNT//21X,8HOXY/N = ,F6.4,10H NIT
     */N  = ,F6.4,1
     50H BUT/N  = ,F7.4,10H  MOLS/MN2/)
   54 FORMAT(21X,31HBUTANE TO OXYGEN MOLAR RATIO = ,F8.4/
     */21X,25HDENSITY
     2 OF GAS MIXTURE = ,F8.4,9H LB/CU FT//21X,15HGAS
     * VELOCITY = ,F6.2,7
     3H FT/SEC //21X,47HRESIDENCE TIME BASED ON ENTRANCE
     * CONDITIONS  = ,
     4F5.2,5H SEC //21X,18HREYNOLDS NUMBER = ,I7)
   93 FORMAT(1H1)
  107 FORMAT(1X,22X,I3,2X,4(2X,F11.6))
  199 FORMAT(28X,30HMOLE PRODUCT PER MOLE N-BUTANE)
  201 FORMAT(/ 20X,2HCO,6X,3HCO2,3X,5HBUTEN,3X,6HPARFIN,2X
     *,6HALCOHL,2X,6
     2HALDHYD,2X,6HOXYGCO,3X,5HWATER)
  203 FORMAT(16X,10F8.4)
  204 FORMAT(28X,31HMOLE PRODUCT PER MOLE N-BUTENES)
  206 FORMAT(28X,24HMOLE PRODUCT PER MOLE CO)
  208 FORMAT(28X,28HMOLE PRODUCT PER MOLE ETHENE)


      PAGE=13

C         READ IN THE CONSTANTS
C

      READ(5,9)NP,NC,NJ,JP,NT
      READ(5,1)(CAR(I),HYD(I),OXY(I),I=1,JP)
      READ(5,2)(RSP(I),CRP(I),I=1,NP)
      READ(5,2)(RSC(I),CRC(I),I=1,NC)
      WRITE(6,93)
      DO 75 LPN=1,NT
      READ(5,6)NRUN,NS

C         READ IN THE INPUT DATA
```

```
          C         CHROMATOGRAPH   ...(CONT'D)
C
      READ(5,4)ARW,BTW,PR,TG


      GSW=ARW+BTW
      ARM=ARW/28.855
      BTM=BTW/58.124
      GSM=ARM+BTM
      ARP=ARM/GSM*100.0
      BTP=BTM/GSM*100.0
      OXP=0.21*ARP
      TNP=0.79*ARP
      OTN=OXP/TNP
      BTN=BTP/TNP
      TTN=TNP/TNP
      TNN=OTN+BTN+TTN
      BTO=BTN/OTN
      XAR=0.01*ARP
      XBT=0.01*BTP
      AVM=28.855*XAR+58.124*XBT
      DG=AVM*PR/(10.73*(460.+TG))
      VEL=GSW/(7.67*DG)
C
C        CALCULATE THE RESIDENCE TIMES
C
      RES=9.75/VEL
      RES=116.0/(12.0*VEL)
      RES1=5.0/(12.0*VEL)
      RES2=30.4/(12.0*VEL)
      RES3=41.1/(12.0*VEL)
      RES4=51.8/(12.0*VEL)
      RES5=62.5/(12.0*VEL)
      RES6=73.5/(12.0*VEL)
      RES7=83.9/(12.0*VEL)
      RES8=94.6/(12.0*VEL)
      RES9=105.3/(12.0*VEL)


      UAR=2.42*(0.0175+0.000019*TG)
      UBT=2.42*(0.0063+0.0000134*TG)
      UG=(5.372*XAR*UAR+7.624*XBT*UBT)/(5.372*XAR+7.624*XBT)
      RN=187.5*VEL*DG/UG
      IRN=RN
      WRITE(6,50)PAGE,NRUN
      WRITE(6,51)
      WRITE(6,53)ARW,BTW,TG,PR,OXP,TNP,BTP,OTN,TTN,BTN
      WRITE(6,54)BTO,DG,VEL,RES,IRN
      WRITE(6,93)
```

```
      C          CHROMATOGRAPH    ...(CONT'D)
      DO 500 LJ=1,NS
      READ(5,9)NSAMP
      PAGE=PAGE+1
      READ(5,5)(PRA(I),I=1,NP)
      READ(5,5)(CHA(I),I=1,NC)
      PRAS=0.0
      PRASM=0.0
      DO 10 I=1,NP
      PRAM(I)=PRA(I)/RSP(I)/CRP(I)
      PRAS=PRAS+PRA(I)
      PRASM=PRASM+PRAM(I)
   10 CONTINUE
      PRAT=0.0
      PRATM=0.0
      DO 11 I=1,NP
      PRAP(I)=PRA(I)/PRAS*100.0
      PRAPM(I)=PRAM(I)/PRASM*100.0
      PRAT=PRAT+PRAP(I)
      PRATM=PRATM+PRAPM(I)
   11 CONTINUE
      CHAS=0.0
      CHASM=0.0
      DO 12 I=1,NC
      CHAM(I)=CHA(I)/RSC(I)/CRC(I)
      CHAS=CHAS+CHA(I)
      CHASM=CHASM+CHAM(I)
   12 CONTINUE
C
C          CALCULATE WT PER CENT AND MOL PER CENT

      DO 13 I=1,NC
      CHAP(I)=CHA(I)/CHAS*100.0
      CHAPM(I)=CHAM(I)/CHASM*100.0
   13 CONTINUE
      TCNT=0.0
      TCNTM=0.0
      DO 14 I=1,NJ
      PCNT(I)=CHAP(I)*PRAP(1)/100.0
      PCNTM(I)=CHAPM(I)*PRAPM(1)/100.0
      TCNT=TCNT+PCNT(I)
      TCNTM=TCNTM+PCNTM(I)
   14 CONTINUE
      DO 15 I=2,NP
      JK=NJ+I-1
      PCNT(JK)=PRAP(I)
      PCNTM(JK)=PRAPM(I)
      TCNT=TCNT+PCNT(JK)
      TCNTM=TCNTM+PCNTM(JK)
   15 CONTINUE
```

```
C                CHROMATOGRAPH   ...(CONT'D)
C
C         MAKE CARBON HYDROGEN AND OXYGEN BALANCES
      TCARB=0.0
      THYDB=0.0
      TOXYB=0.0
      TRPN=0.0
      DO 26 I=1,JP
      RPN(I)=PCNTM(I)/PCNTM(3)
      CARB(I)=RPN(I)*CAR(I)
      HYDB(I)=RPN(I)*HYD(I)
      OXYB(I)=RPN(I)*OXY(I)
      TCARB=TCARB+CARB(I)
      THYDB=THYDB+HYDB(I)
      TOXYB=TOXYB+OXYB(I)
      TRPN=TRPN+RPN(I)
   26 CONTINUE
      PCARB=TCARB/(4.0*BTN)*100.0
      POXYB=TOXYB/(2.0*OTN)*100.0
      PHYDB=THYDB/(10.0*BTN)*100.0
      OXRTN=(OTN-RPN(2))/OTN*100.0
      BTRTN=(BTN-RPN(13))/BTN*100.0
      OXRT=OTN-RPN(2)
      BTRT=BTN-RPN(13)
C
C         CALCULATE SELECTIVITIES
C
C         PRODUCTS FORMED PER MOLE BUTANE AND
C         OXYGEN REACTED
      RPT=0.0
      RPO=0.0
      DO 27 I=1,JP
      RPTOX(I)=RPN(I)/OXRT
      RPTBT(I)=RPN(I)/BTRT
      RPT=RPT+RPTBT(I)
      RPO=RPO+RPTOX(I)
   27 CONTINUE
      WRITE(6,29)PAGE,NRUN,NSAMP
      WRITE(6,32)
      DO 73 I=1,JP
      WRITE(6,107)I,PCNTM(I),RPN(I),RPTOX(I),RPTBT(I)
   73 CONTINUE
      WRITE(6,38)TCNT,TCNTM,TRPN,TCARB,PCARB,THYDB,PHYDB
     *,TOXYB,POXYB,OXR
     2TN,BTRTN
      RPT=RPT-RPTBT(2)-RPTBT(3)-RPTBT(13)
      RPO=RPO-RPTOX(2)-RPTOX(3)-RPTOX(13)
```

```
      C          CHROMATOGRAPH   ...(CONT'D)
         CRTN=0.0
         ORTN=0.0
         OOXPR=0.0
         BOXPR=0.0
         DO 71  I=18,JP
         BOXPR=BOXPR+RPTBT(I)
         OOXPR=OOXPR+RPTOX(I)
         ORTN=ORTN+RPN(I)
      71 CONTINUE
         CRPR=0.0
         OXPR=0.0
         DO 72  I=5,15
         CRPR=CRPR+RPTBT(I)
         OXPR=OXPR+RPTOX(I)
         CRTN=CRTN+RPN(I)
      72 CONTINUE
         CRPR=CRPR-RPTBT(13)+RPTBT(1)
         OXPR=OXPR-RPTOX(13)+RPTOX(1)
         CRTN=CRTN-RPN(13)+RPN(1)
C
C            PER CENT N-BUTANE REACTED TO DIFFERENT PRODUCTS

         COCO2=(RPTBT(4)+RPTBT(16))/RPT*100.0
         OLEF=(RPTBT(6)+RPTBT(9)+RPTBT(11)+RPTBT(12))/RPT*100.0
         PARL=(RPTBT(5)+RPTBT(7)+RPTBT(8))/RPT*100.0
         H2O=RPTBT(17)/RPT*100.0
         ALKET=RPTBT(23)+RPTBT(28)+RPTBT(30)
         ALDE=RPTBT(18)+RPTBT(20)+RPTBT(24)+RPTBT(27)
         ALCO=RPTBT(19)+RPTBT(21)+RPTBT(26)+RPTBT(29)
         DEHYD=RPTBT(6)+RPTBT(9)+RPTBT(11)+RPTBT(12)
         CRACK=RPTBT(5)+RPTBT(7)+RPTBT(8)+RPTBT(1)
         OXYG=0.0
         DO 79 KK=18,JP
         OXYG=OXYG+RPTBT(KK)
      79 CONTINUE
         OXYGE=OXYG
         OXYG=OXYG/RPT*100.0


         BUTEN=RPTBT(11)+RPTBT(12)
         CO=RPTBT(4)
         CO2=RPTBT(16)
         WATER=RPTBT(17)
         X1=CRACK
         X2=OXYGE
         X3=ALCO
         X4=ALDE
         X5=ALKET
         Y1=BUTEN
```

```
C          CHROMATOGRAPH   ...(CONT'D)
      Y2=DEHYD
      Y3=CO
      Y4=WATER
      Y5=RPTBT(6)
      WRITE(6,201)
      WRITE(6,199)
      WRITE(6,203)CO,CO2,BUTEN,CRACK,ALCO,ALDE,OXYGE,WATER
C
C          MOLE PRODUCT PER MOLE BUTENES
C
      CO=CO/Y1
      CO2=CO2/Y1
      BUTEN=BUTEN/Y1
      DEHYD=DEHYD/Y1
      CRACK=CRACK/Y1
      ALCO=ALCO/Y1
      ALDE=ALDE/Y1
      ALKET=ALKET/Y1
      OXYGE=OXYGE/Y1
      WATER=WATER/Y1
      WRITE(6,204)
      WRITE(6,203)CO,CO2,BUTEN,CRACK,ALCO,ALDE,OXYGE,WATER
C
C          MOLE  RODUCT PER MOLE OLEFINS
C
      CO=RPTBT(4)/Y2
      CO2=RPTBT(16)/Y2
      BUTEN=Y1/Y2
      DEHYD=Y2/Y2
      CRACK=X1/Y2
      ALCO=X3/Y2
      ALDE=X4/Y2
      ALKET=X5/Y2
      OXYGE=X2/Y2
      WATER=Y4/Y2
C
C          MOLE PRODUCT PER MOLE CARBON MONOXIDE
C
      CO=RPTBT(4)/Y3
      CO2=RPTBT(16)/Y3
      BUTEN=Y1/Y3
      DEHYD=Y2/Y3
      CRACK=X1/Y3
      ALCO=X3/Y3
      ALDE=X4/Y3
      ALKET=X5/Y3
      OXYGE=X2/Y3
```

```
C              CHROMATOGRAPH   ...(CONT'D)
      WATER=Y4/Y3
      WRITE(6,206)
      WRITE(6,203)CO,CO2,BUTEN,CRACK,ALCO,ALDE,OXYGE,WATER
C         MOLE PRODUCT PER MOLE WATER
C

      CO=RPTBT(4)/Y4
      CO2=RPTBT(16)/Y4
      BUTEN=Y1/Y4
      DEHYD=Y2/Y4
      CRACK=X1/Y4
      ALCO=X3/Y4
      ALDE=X4/Y4
      ALKET=X5/Y4
      OXYGE=X2/Y4
      WATER=Y4/Y4
C         MOLE PRODUCT PER MOLE ETHYLENE
C

      CO=RPTBT(4)/Y5
      CO2=RPTBT(16)/Y5
      BUTEN=Y1/Y5
      DEHYD=Y2/Y5
      CRACK=X1/Y5
      ALCO=X3/Y5
      ALDE=X4/Y5
      ALKET=X5/Y5
      OXYGE=X2/Y5
      WATER=Y4/Y5
      WRITE(6,208)
      WRITE(6,203)CO,CO2,BUTEN,CRACK,ALCO,ALDE,OXYGE,WATER
      WRITE(6,93)
  500 CONTINUE
   75 CONTINUE
      CALL EXIT
      END
```

72 12.06.41

```
RUN NO =  60
REACTOR ENTRANCE CONDITIONS


AIR =   1.68 LB/HR             BUTANE =   9.90 LB/HR
TEMPERATURE =   685.00 DEG F
PRESSURE =  53.60 LB/SQ IN
OXYGEN = 5.3497 NITROGEN = 20.1251 BUTANE = 74.5251  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N   =  3.7030  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =  13.9306
DENSITY OF GAS MIXTURE =   0.2210 LB/CU FT
GAS VELOCITY =   6.83 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.41 SEC
REYNOLDS NUMBER =    6358
```

```
RUN NO =   60   SAMPLE NO =   1

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1       0.000000       0.000000       0.000000       0.000000
    2       4.393529       0.222142       5.085697      17.492111
    3      19.777946       1.000000      22.893814      78.742614
    4       0.057071       0.002885       0.066062       0.227220
    5       0.019322       0.000976       0.022366       0.076928
    6       0.017625       0.000891       0.020401       0.070171
    7       0.000000       0.000000       0.000000       0.000000
    8       0.015184       0.000767       0.017576       0.060455
    9       0.753493       0.038097       0.872200       2.999909
   10       0.202902       0.010259       0.234868       0.807824
   11       0.033678       0.001702       0.038984       0.134085
   12       0.026014       0.001315       0.030112       0.103570
   13      72.988403       3.690393      84.487182     290.591186
   14       0.000000       0.000000       0.000000       0.000000
   15       0.000000       0.000000       0.000000       0.000000
   16       0.142664       0.007213       0.165140       0.567996
   17       0.659517       0.033346       0.763419       2.625760
   18       0.264578       0.013377       0.306260       1.053374
   19       0.084625       0.004278       0.097957       0.336920
   20       0.097405       0.004924       0.112751       0.387805
   21       0.000000       0.000000       0.000000       0.000000
   22       0.404339       0.020443       0.468039       1.609808
   23       0.000000       0.000000       0.000000       0.000000
   24       0.028200       0.001425       0.032642       0.112273
   25       0.033605       0.001699       0.038899       0.133792
   26       0.000000       0.000000       0.000000       0.000000
   27       0.000000       0.000000       0.000000       0.000000
   28       0.000000       0.000000       0.000000       0.000000
   29       0.000000       0.000000       0.000000       0.000000
   30       0.000000       0.000000       0.000000       0.000000

 TOTALS   099.999999     100.000015       5.056138

CARBON   BALANCE    15.021898 LB AT/MOLN2.    101.41 PERCENT
HYDROGEN BALANCE    37.503631 LB AT/MOLN2.    101.27 PERCENT
OXYGEN BALANCE       0.541093 LB AT/MOLN2.    101.77 PERCENT

PERCENT O2 REACT     16.4319     PERCENT C4 REACT      0.3429

  CO       CO2    BUTEN   PARFIN  ALCOHL  ALDHYD  OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.2272  0.5679  0.2376  0.1373  0.3369  1.5534  3.6339  2.6257
          MOLE PRODUCT PER MOLE N-BUTENES
0.9560  2.3899  1.0000  0.5780  1.4176  6.5365 15.2908 11.0485
          MOLE PRODUCT PER MOLE CO
1.0000  2.4997  1.0459  0.6046  1.4827  6.8367 15.9931 11.5559
          MOLE PRODUCT PER MOLE ETHENE
3.2380  8.0944  3.3868  1.9578  4.8014 22.1380 51.7873 37.4193
```

```
RUN NO =  60  SAMPLE NO =  2

 PRD NO  MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1      0.000000      0.000000      0.000000      0.000000
    2      4.245702      0.213955      4.125055      3.401256
    3     19.843860      1.000000     19.279968     15.897029
    4      0.212200      0.010693      0.206170      0.169995
    5      0.036646      0.001846      0.035604      0.029357
    6      0.025004      0.001260      0.024294      0.020031
    7      0.000000      0.000000      0.000000      0.000000
    8      0.029757      0.001499      0.028912      0.023839
    9      0.842347      0.042448      0.818411      0.674809
   10      0.188586      0.009503      0.183227      0.151077
   11      0.123838      0.006240      0.120319      0.099207
   12      0.180045      0.009073      0.174929      0.144235
   13     72.235382      3.640188     70.182708     57.868171
   14      0.000000      0.000000      0.000000      0.000000
   15      0.000000      0.000000      0.000000      0.000000
   16      0.198074      0.009981      0.192446      0.158678
   17      0.614352      0.030959      0.596894      0.492161
   18      0.360341      0.018158      0.350102      0.288671
   19      0.270962      0.013654      0.263262      0.217069
   20      0.089848      0.004527      0.087294      0.071977
   21      0.043085      0.002171      0.041861      0.034516
   22      0.390205      0.019663      0.379116      0.312595
   23      0.000000      0.000000      0.000000      0.000000
   24      0.029757      0.001499      0.028912      0.023839
   25      0.040172      0.002024      0.039031      0.032182
   26      0.000000      0.000000      0.000000      0.000000
   27      0.000000      0.000000      0.000000      0.000000
   28      0.000000      0.000000      0.000000      0.000000
   29      0.000000      0.000000      0.000000      0.000000
   30      0.000000      0.000000      0.000000      0.000000

 TOTALS   99.999984    100.000091      5.039344

CARBON   BALANCE    14.912012 LB AT/MOLN2.    100.67 PERCENT
HYDROGEN BALANCE    37.182304 LB AT/MOLN2.    100.40 PERCENT
OXYGEN BALANCE       0.551227 LB AT/MOLN2.    103.68 PERCENT

PERCENT O2 REACT     19.5119    PERCENT C4 REACT      1.6987

  CO      CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.1699  0.1586   0.2434   0.0531   0.2515   0.3844   0.9808   0.4921
          MOLE PRODUCT PER MOLE N-BUTENES
0.6982  0.6518   1.0000   0.2185   1.0334   1.5793   4.0290   2.0216
          MOLE PRODUCT PER MOLE CO
1.0000  0.9334   1.4320   0.3129   1.4799   2.2617   5.7698   2.8951
          MOLE PRODUCT PER MOLE ETHENE
8.4864  7.9214  12.1530   2.6556  12.5595  19.1942  48.9656  24.5694
```

```
RUN NO =  60   SAMPLE NO =   3

  PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
     1        0.141659      0.007061      0.028775      0.018580
     2        0.409908      0.020432      0.083265      0.053763
     3       20.061649      1.000000      4.075140      2.631281
     4        1.927261      0.096066      0.391486      0.252779
     5        0.465459      0.023201      0.094549      0.061049
     6        0.495489      0.024698      0.100649      0.064988
     7        0.145908      0.007273      0.029638      0.019137
     8        0.214827      0.010708      0.043638      0.028176
     9        2.130676      0.106206      0.432806      0.279458
    10        0.168916      0.008419      0.034312      0.022155
    11        1.305461      0.065072      0.265179      0.171223
    12        0.366641      0.018275      0.074476      0.048088
    13       66.665863      3.323050     13.541894      8.743877
    14        0.034748      0.001732      0.007058      0.004557
    15        0.019819      0.000987      0.004025      0.002599
    16        0.341587      0.017026      0.069386      0.044802
    17        1.206030      0.060116      0.244982      0.158182
    18        0.161538      0.008052      0.032813      0.021187
    19        2.289994      0.114147      0.465168      0.300355
    20        0.432166      0.021541      0.087786      0.056682
    21        0.144930      0.007224      0.029439      0.019009
    22        0.325910      0.016245      0.066202      0.042746
    23        0.010999      0.000548      0.002234      0.001442
    24        0.199152      0.009927      0.040454      0.026120
    25        0.105573      0.005262      0.021445      0.013846
    26        0.010360      0.000516      0.002104      0.001358
    27        0.017845      0.000889      0.003625      0.002340
    28        0.008511      0.000424      0.001729      0.001116
    29        0.168864      0.008417      0.034301      0.022148
    30        0.022410      0.001117      0.004552      0.002939

   TOTALS    99.999923    099.999999      4.984634

CARBON    BALANCE    14.529146 LB AT/MOLN2.     98.08 PERCENT
HYDROGEN BALANCE     35.979316 LB AT/MOLN2.     97.16 PERCENT
OXYGEN BALANCE        0.425415 LB AT/MOLN2.     80.01 PERCENT

PERCENT O2 REACT     92.3135     PERCENT C4 REACT      10.2628

  CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2527   0.0448   0.2193   0.1269   0.3428   0.1063   0.5112   0.1581
          MOLE  PRODUCT  PER MOLE  N-BUTENES
1.1525   0.2042   1.0000   0.5788   1.5633   0.4848   2.3313   0.7212
          MOLE  PRODUCT  PER MOLE  CO
1.0000   0.1772   0.8676   0.5021   1.3564   0.4206   2.0226   0.6257
          MOLE  PRODUCT  PER MOLE  ETHENE
3.8896   0.6893   3.3746   1.9533   5.2758   1.6361   7.8674   2.4340
```

```
    RUN NO =   60   SAMPLE NO =   4

     PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
        1       0.226197       0.011307       0.044903       0.027204
        2       0.279954       0.013995       0.055574       0.033669
        3      20.003654       1.000000       3.970971       2.405771
        4       2.467779       0.123366       0.489884       0.296791
        5       0.895498       0.044766       0.177767       0.107698
        6       0.769117       0.038448       0.152679       0.092499
        7       0.307392       0.015366       0.061021       0.036969
        8       0.226652       0.011330       0.044993       0.027258
        9       2.364611       0.118208       0.469404       0.284383
       10       0.129199       0.006458       0.025647       0.015538
       11       0.569943       0.028491       0.113140       0.068545
       12       0.624766       0.031232       0.124023       0.075138
       13      65.760528       3.287425      13.054271       7.908795
       14       0.094914       0.004744       0.018841       0.011415
       15       0.066852       0.003342       0.013271       0.008040
       16       0.811726       0.040578       0.161137       0.097623
       17       1.495604       0.074766       0.296895       0.179871
       18       0.418364       0.020914       0.083050       0.050315
       19       1.277353       0.063856       0.253570       0.153622
       20       0.307709       0.015382       0.061084       0.037007
       21       0.149565       0.007476       0.029690       0.017987
       22       0.285472       0.014270       0.056669       0.034332
       23       0.015115       0.000755       0.003000       0.001817
       24       0.140824       0.007039       0.027955       0.016936
       25       0.053079       0.002653       0.010537       0.006383
       26       0.025628       0.001281       0.005087       0.003082
       27       0.021128       0.001056       0.004194       0.002541
       28       0.029476       0.001473       0.005851       0.003545
       29       0.169748       0.008485       0.033697       0.020415
       30       0.012318       0.000615       0.002445       0.001481

     TOTALS   100.000015     099.999999       4.999088

 CARBON   BALANCE     14.398527 LB AT/MOLN2.    97.20 PERCENT
 HYDROGEN BALANCE     35.552436 LB AT/MOLN2.    96.00 PERCENT
 OXYGEN BALANCE        0.452543 LB AT/MOLN2.    85.12 PERCENT

 PERCENT O2 REACT     94.7351     PERCENT C4 REACT     11.2248

   CO        CO2    BUTEN   PARFIN  ALCOHL  ALDHYD  OXYGCO   WATER
            MOLE PRODUCT PER MOLE N-BUTANE
 0.2967   0.0976  0.1436  0.1991  0.1951  0.1067  0.3494  0.1798
            MOLE PRODUCT PER MOLE N-BUTENES
 2.0655   0.6794  1.0000  1.3858  1.3579  0.7432  2.4322  1.2518
            MOLE PRODUCT PER MOLE CO
 1.0000   0.3289  0.4841  0.6709  0.6573  0.3598  1.1774  0.6060
            MOLE PRODUCT PER MOLE ETHENE
 3.2085   1.0553  1.5533  2.1527  2.1092  1.1546  3.7780  1.9445
```

```
RUN NO =  61
REACTOR ENTRANCE CONDITIONS


AIR =   2.02 LB/HR           BUTANE =   9.50 LB/HR
TEMPERATURE =   695.00 DEG F
PRESSURE =  53.70 LB/SQ IN
OXYGEN = 6.2973 NITROGEN = 23.6900 BUTANE = 70.0126  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.9553  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =  11.1177
DENSITY OF GAS MIXTURE =   0.2138 LB/CU FT
GAS VELOCITY =   7.02 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.37 SEC
REYNOLDS NUMBER =    6088
```

```
RUN NO =  61   SAMPLE NO =  1

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1        0.000000      0.000000      0.000000      0.000000
    2        5.429907      0.232142      6.892628     14.317525
    3       23.390373      1.000000     29.691326     61.675506
    4        0.029565      0.001264      0.037530      0.077958
    5        0.000000      0.000000      0.000000      0.000000
    6        0.008554      0.000365      0.010858      0.022556
    7        0.004910      0.000209      0.006233      0.012948
    8        0.008347      0.000356      0.010596      0.022011
    9        0.997943      0.042664      1.266772      2.631368
   10        0.205517      0.008786      0.260879      0.541905
   11        0.046349      0.001981      0.058834      0.122212
   12        0.044045      0.001883      0.055910      0.116137
   13       68.747787      2.939148     87.267211    181.273468
   14        0.000000      0.000000      0.000000      0.000000
   15        0.000000      0.000000      0.000000      0.000000
   16        0.121740      0.005204      0.154535      0.321005
   17        0.100983      0.004317      0.128186      0.266271
   18        0.237484      0.010153      0.301458      0.626197
   19        0.111901      0.004784      0.142045      0.295060
   20        0.061248      0.002618      0.077747      0.161499
   21        0.014772      0.000631      0.018752      0.038952
   22        0.418164      0.017877      0.530810      1.102612
   23        0.000000      0.000000      0.000000      0.000000
   24        0.008674      0.000370      0.011010      0.022871
   25        0.011869      0.000507      0.015067      0.031297
   26        0.000000      0.000000      0.000000      0.000000
   27        0.000000      0.000000      0.000000      0.000000
   28        0.000000      0.000000      0.000000      0.000000
   29        0.000000      0.000000      0.000000      0.000000
   30        0.000000      0.000000      0.000000      0.000000

 TOTALS    099.999999    100.000045      4.275264

CARBON   BALANCE    12.003705 LB AT/MOLN2.    101.54 PERCENT
HYDROGEN BALANCE    29.910942 LB AT/MOLN2.    101.20 PERCENT
OXYGEN BALANCE       0.517219 LB AT/MOLN2.     97.28 PERCENT

PERCENT O2 REACT      12.6700     PERCENT C4 REACT      0.5486

  CO       CO2    BUTEN   PARFIN  ALCOHL  ALDHYD   OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.0779  0.3210  0.2383  0.0349  0.3340  0.8105  2.2784  0.2662
          MOLE PRODUCT PER MOLE N-BUTENES
0.3270  1.3467  1.0000  0.1466  1.4013  3.4007  9.5594  1.1171
          MOLE PRODUCT PER MOLE CO
1.0000  4.1176  3.0574  0.4484  4.2845 10.3974 29.2270  3.4155
          MOLE PRODUCT PER MOLE ETHENE
3.4561 14.2312 10.5668  1.5498 14.8079 35.9352101.0133 11.8047
```

```
RUN NO =   61   SAMPLE NO =   3

  PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MOBUT R
     1        0.342900       0.015092       0.059797       0.041731
     2        0.304917       0.013421       0.053173       0.037109
     3       22.719348       1.000000       3.961939       2.764998
     4        2.687829       0.118305       0.468720       0.327115
     5        1.214770       0.053468       0.211839       0.147840
     6        1.478911       0.065094       0.257901       0.179987
     7        0.422261       0.018585       0.073636       0.051390
     8        0.148640       0.006542       0.025920       0.018089
     9        1.590097       0.069988       0.277290       0.193518
    10        0.105422       0.004640       0.018384       0.012830
    11        1.310266       0.057671       0.228492       0.159462
    12        0.674069       0.029669       0.117548       0.082035
    13       58.927146       2.593698      10.276077       7.171573
    14        0.000000       0.000000       0.000000       0.000000
    15        0.076276       0.003357       0.013301       0.009282
    16        0.461047       0.020293       0.080400       0.056110
    17        3.674382       0.161729       0.640761       0.447181
    18        0.336667       0.014818       0.058710       0.040973
    19        2.048395       0.090160       0.357211       0.249294
    20        0.384697       0.016932       0.067085       0.046818
    21        0.086387       0.003802       0.015064       0.010513
    22        0.367920       0.016194       0.064160       0.044776
    23        0.074029       0.003258       0.012909       0.009009
    24        0.142382       0.006267       0.024829       0.017328
    25        0.093565       0.004118       0.016316       0.011387
    26        0.021443       0.000943       0.003739       0.002609
    27        0.020146       0.000886       0.003513       0.002451
    28        0.033295       0.001465       0.005806       0.004052
    29        0.232569       0.010236       0.040556       0.028304
    30        0.020382       0.000897       0.003554       0.002480

   TOTALS     99.999954    100.000030       4.401533

CARBON   BALANCE    11.628322 LB AT/MOLN2.     98.36 PERCENT
HYDROGEN BALANCE    28.906322 LB AT/MOLN2.     97.80 PERCENT
OXYGEN BALANCE       0.517444 LB AT/MOLN2.     97.32 PERCENT

PERCENT O2 REACT     94.9511     PERCENT C4 REACT     12.2375

   CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.3271   0.0561   0.2414   0.2590   0.2907   0.1075   0.4699   0.4471
           MOLE  PRODUCT  PER MOLE  N-BUTENES
1.3545   0.2323   1.0000   1.0726   1.2038   0.4454   1.9461   1.8516
           MOLE  PRODUCT  PER MOLE  CO
1.0000   0.1715   0.7382   0.7919   0.8887   0.3288   1.4368   1.3670
           MOLE  PRODUCT  PER MOLE  ETHENE
1.8174   0.3117   1.3417   1.4392   1.6152   0.5976   2.6112   2.4845
```

```
RUN NO =  61   SAMPLE NO =   4

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1        0.290236      0.012949      0.051272      0.031836
    2        0.297002      0.013251      0.052467      0.032578
    3       22.412090      1.000000      3.959286      2.458413
    4        2.799656      0.124917      0.494583      0.307098
    5        1.362700      0.060802      0.240732      0.149476
    6        1.238020      0.055238      0.218706      0.135800
    7        0.475003      0.021194      0.083913      0.052103
    8        0.217859      0.009720      0.038486      0.023897
    9        3.050521      0.136110      0.538900      0.334615
   10        0.130753      0.005834      0.023098      0.014342
   11        1.329207      0.059307      0.234815      0.145802
   12        0.995022      0.044396      0.175779      0.109145
   13       57.119361      2.548596     10.090620      6.265502
   14        0.000000      0.000000      0.000000      0.000000
   15        0.094790      0.004229      0.016745      0.010397
   16        0.853443      0.038079      0.150768      0.093615
   17        3.784926      0.168878      0.668639      0.415173
   18        0.287751      0.012839      0.050833      0.031563
   19        1.865853      0.083252      0.329618      0.204668
   20        0.362083      0.016155      0.063965      0.039717
   21        0.168906      0.007536      0.029838      0.018527
   22        0.319808      0.014269      0.056496      0.035080
   23        0.034578      0.001542      0.006108      0.003792
   24        0.119924      0.005350      0.021185      0.013154
   25        0.080919      0.003610      0.014295      0.008876
   26        0.026755      0.001193      0.004726      0.002934
   27        0.020550      0.000916      0.003630      0.002254
   28        0.048357      0.002157      0.008542      0.005304
   29        0.194145      0.008662      0.034297      0.021296
   30        0.019895      0.000887      0.003514      0.002182

 TOTALS     99.999969     99.999984      4.461873

CARBON    BALANCE    11.729370 LB AT/MOLN2.     99.22 PERCENT
HYDROGEN BALANCE    29.001487 LB AT/MOLN2.     98.13 PERCENT
OXYGEN BALANCE       0.554834 LB AT/MOLN2.    104.36 PERCENT

PERCENT O2 REACT     95.0147    PERCENT C4 REACT     13.7636

  CO         CO2    BUTEN    PARFIN   ALCOHL  ALDHYD   OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.3070    0.0936   0.2549   0.2573   0.2474  0.0866   0.3893   0.4151
            MOLE  PRODUCT  PER MOLE  N-BUTENES
1.2045    0.3671   1.0000   1.0092   0.9704  0.3400   1.5271   1.6284
            MOLE  PRODUCT  PER MOLE  CO
1.0000    0.3048   0.8301   0.8378   0.8056  0.2822   1.2678   1.3519
            MOLE  PRODUCT  PER MOLE  ETHENE
2.2613    0.6893   1.8773   1.8947   1.8219  0.6383   2.8671   3.0572
```

```
RUN NO =  62
REACTOR ENTRANCE CONDITIONS


AIR =    2.60 LB/HR             BUTANE =   9.60 LB/HR
TEMPERATURE =   695.00 DEG F
PRESSURE =  53.70 LB/SQ IN
OXYGEN = 7.4126 NITROGEN = 27.8855 BUTANE = 64.7017  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.3202  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   8.7285
DENSITY OF GAS MIXTURE =   0.2070 LB/CU FT
GAS VELOCITY =   7.68 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.25 SEC
REYNOLDS NUMBER =    6223
```

```
RUN NO =  62   SAMPLE NO =  1

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1       0.000000       0.000000       0.000000       0.000000
    2       5.918601       0.221237       4.962115       5.955798
    3      26.752258       1.000000      22.428909      26.920387
    4       0.299170       0.011182       0.250822       0.301050
    5       0.040817       0.001525       0.034221       0.041074
    6       0.019715       0.000736       0.016529       0.019839
    7       0.004123       0.000154       0.003457       0.004149
    8       0.018926       0.000707       0.015867       0.019045
    9       2.586965       0.096700       2.168893       2.603223
   10       0.184649       0.006902       0.154808       0.185809
   11       0.156108       0.005835       0.130880       0.157089
   12       0.019684       0.000735       0.016503       0.019808
   13      61.078392       2.283112      51.207702      61.462249
   14       0.000000       0.000000       0.000000       0.000000
   15       0.000000       0.000000       0.000000       0.000000
   16       1.774366       0.066325       1.487616       1.785517
   17       0.176376       0.006592       0.147872       0.177485
   18       0.402461       0.015044       0.337421       0.404990
   19       0.088349       0.003302       0.074072       0.088905
   20       0.068041       0.002543       0.057045       0.068468
   21       0.010826       0.000404       0.009076       0.010894
   22       0.341729       0.012773       0.286503       0.343877
   23       0.000000       0.000000       0.000000       0.000000
   24       0.026286       0.000982       0.022038       0.026452
   25       0.032201       0.001203       0.026997       0.032403
   26       0.000000       0.000000       0.000000       0.000000
   27       0.000000       0.000000       0.000000       0.000000
   28       0.000000       0.000000       0.000000       0.000000
   29       0.000000       0.000000       0.000000       0.000000
   30       0.000000       0.000000       0.000000       0.000000

TOTALS     99.999984      99.999954       3.738000

CARBON   BALANCE      9.615722 LB AT/MOLN2.    103.60 PERCENT
HYDROGEN BALANCE     23.681831 LB AT/MOLN2.    102.06 PERCENT
OXYGEN BALANCE        0.629156 LB AT/MOLN2.    118.34 PERCENT

PERCENT O2 REACT      16.7725     PERCENT C4 REACT      1.6009

   CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
 0.3010   1.7855   0.1768   0.0642   0.0997   0.4999   0.9759   0.1774
           MOLE  PRODUCT  PER MOLE  N-BUTENES
 1.7018  10.0934   1.0000   0.3633   0.5641   2.8259   5.5172   1.0033
           MOLE  PRODUCT  PER MOLE  CO
 1.0000   5.9309   0.5876   0.2134   0.3315   1.6605   3.2419   0.5895
           MOLE  PRODUCT  PER MOLE  ETHENE
15.1746  90.0000   8.9166   3.2395   5.0304  25.1983  49.1954   8.9462
```

```
    RUN NO =   62   SAMPLE NO =   2

      PRD NO    MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
         1         0.000000       0.000000       0.000000       0.000000
         2         5.500148       0.200303       3.057165       2.584755
         3        27.459079       1.000000      15.262672      12.904201
         4         0.456546       0.016626       0.253763       0.214550
         5         0.044149       0.001607       0.024539       0.020747
         6         0.123902       0.004512       0.068869       0.058227
         7         0.024307       0.000885       0.013511       0.011423
         8         0.041489       0.001510       0.023061       0.019497
         9         1.761894       0.064164       0.979319       0.827989
        10         0.156685       0.005706       0.087091       0.073633
        11         0.1742[illegible]4       0.006345       0.096856       0.081889
        12         0.225349       0.008206       0.125256       0.105901
        13        61.584236       2.242764      34.230575      28.941078
        14         0.025976       0.000946       0.014438       0.012207
        15         0.000000       0.000000       0.000000       0.000000
        16         0.480655       0.017504       0.267164       0.225880
        17         0.807087       0.029392       0.448606       0.379285
        18         0.137898       0.005021       0.076648       0.064804
        19         0.308253       0.011225       0.171337       0.144861
        20         0.127580       0.004646       0.070913       0.059955
        21         0.052523       0.001912       0.029194       0.024683
        22         0.294048       0.010708       0.163441       0.138185
        23         0.000000       0.000000       0.000000       0.000000
        24         0.055371       0.002016       0.030777       0.026021
        25         0.053000       0.001930       0.029459       0.024907
        26         0.000000       0.000000       0.000000       0.000000
        27         0.000000       0.000000       0.000000       0.000000
        28         0.000000       0.000000       0.000000       0.000000
        29         0.097062       0.003534       0.053950       0.045613
        30         0.008643       0.000314       0.004804       0.004062

     TOTALS       99.999984     100.000045       3.641783

CARBON   BALANCE      9.378070 LB AT/MOLN2.    101.04 PERCENT
HYDROGEN BALANCE     23.287170 LB AT/MOLN2.    100.36 PERCENT
OXYGEN BALANCE        0.522945 LB AT/MOLN2.     98.36 PERCENT

PERCENT O2 REACT      24.6477     PERCENT C4 REACT       3.3398

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD    OXYGCO     WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2145   0.2258   0.1877   0.0516   0.2151   0.1507    0.5330    0.3792
           MOLE  PRODUCT  PER MOLE  N-BUTENES
1.1424   1.2028   1.0000   0.2751   1.1457   0.8029    2.8387    2.0197
           MOLE  PRODUCT  PER MOLE  CO
1.0000   1.0528   0.8752   0.2408   1.0028   0.7027    2.4846    1.7678
           MOLE  PRODUCT  PER MOLE  ETHENE
3.6847   3.8793   3.2251   0.8873   3.6951   2.5895    9.1554    6.5139
```

```
RUN NO =  62  SAMPLE NO =  3

PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
  1        0.417555       0.015330       0.064913       0.051651
  2        0.807447       0.029646       0.125526       0.099880
  3       27.236026       1.000000       4.234122       3.369086
  4        2.663660       0.097799       0.414093       0.329493
  5        1.260069       0.046264       0.195890       0.155870
  6        1.247298       0.045795       0.193905       0.154290
  7        0.378621       0.013901       0.058860       0.046835
  8        0.193332       0.007098       0.030055       0.023915
  9        1.578735       0.057964       0.245430       0.195288
 10        0.131572       0.004830       0.020454       0.016275
 11        0.520240       0.019101       0.080876       0.064353
 12        1.009798       0.037075       0.156983       0.124911
 13       55.110519       2.023442       8.567501       6.817151
 14        0.026758       0.000982       0.004159       0.003309
 15        0.021455       0.000787       0.003335       0.002654
 16        0.461883       0.016958       0.071804       0.057134
 17        3.720885       0.136616       0.578450       0.460272
 18        0.216666       0.007955       0.033683       0.026801
 19        1.578055       0.057939       0.245324       0.195204
 20        0.599680       0.022017       0.093226       0.074180
 21        0.106178       0.003898       0.016506       0.013134
 22        0.285468       0.010481       0.044379       0.035312
 23        0.023165       0.000850       0.003601       0.002865
 24        0.121835       0.004473       0.018940       0.015070
 25        0.062258       0.002285       0.009678       0.007701
 26        0.020142       0.000739       0.003131       0.002491
 27        0.026465       0.000971       0.004114       0.003273
 28        0.006853       0.000251       0.001065       0.000847
 29        0.141234       0.005185       0.021956       0.017470
 30        0.026344       0.000967       0.004095       0.003258

  TOTALS     99.999954     100.000045      3.671608

CARBON    BALANCE     9.016687 LB AT/MOLN2.     97.15 PERCENT
HYDROGEN BALANCE     22.439113 LB AT/MOLN2.     96.70 PERCENT
OXYGEN BALANCE        0.445642 LB AT/MOLN2.     83.82 PERCENT

PERCENT O2 REACT     88.8473     PERCENT C4 REACT      12.7923

  CO        CO2     BUTEN    PARFIN   ALCOHL   ALDHYD    OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.3294    0.0571   0.1892   0.2782   0.2283   0.1193    0.3976   0.4602
            MOLE  PRODUCT  PER MOLE  N-BUTENES
1.7409    0.3018   1.0000   1.4702   1.2062   0.6304    2.1008   2.4318
            MOLE  PRODUCT  PER MOLE  CO
1.0000    0.1734   0.5744   0.8445   0.6928   0.3621    1.2067   1.3969
            MOLE  PRODUCT  PER MOLE  ETHENE
2.1355    0.3703   1.2266   1.8035   1.4796   0.7733    2.5770   2.9831
```

```
RUN NO =  62  SAMPLE NO =  4

  PRD NO  MOL PERCENT   MOLS/MOL N2    MOLS/MOXY R   MOLS/MBUT R
     1      0.445837      0.016676      0.066187      0.046648
     2      0.370628      0.013863      0.055021      0.038779
     3     26.734516      1.000000      3.968893      2.797252
     4      3.324902      0.124367      0.493600      0.347887
     5      1.987010      0.074323      0.294983      0.207902
     6      1.446426      0.054103      0.214730      0.151340
     7      0.567226      0.021216      0.084207      0.059349
     8      0.202701      0.007582      0.030092      0.021208
     9      2.567250      0.096027      0.381123      0.268613
    10      0.127131      0.004755      0.018873      0.013301
    11      0.766694      0.028678      0.113820      0.080219
    12      0.705782      0.026399      0.104777      0.073846
    13     52.473564      1.962764      7.790001      5.490348
    14      0.028552      0.001068      0.004238      0.002987
    15      0.018734      0.000700      0.002781      0.001960
    16      0.407629      0.015247      0.060514      0.042650
    17      4.620081      0.172813      0.685877      0.483402
    18      0.335081      0.012533      0.049744      0.035059
    19      1.661945      0.062164      0.246725      0.173890
    20      0.446314      0.016694      0.066258      0.046698
    21      0.111828      0.004182      0.016601      0.011700
    22      0.164753      0.006162      0.024458      0.017238
    23      0.033393      0.001249      0.004957      0.003493
    24      0.116568      0.004360      0.017305      0.012196
    25      0.064431      0.002410      0.009565      0.006741
    26      0.017513      0.000655      0.002599      0.001832
    27      0.027410      0.001025      0.004069      0.002867
    28      0.023207      0.000868      0.003445      0.002428
    29      0.175981      0.006582      0.026125      0.018413
    30      0.027124      0.001014      0.004026      0.002838

  TOTALS     99.999984    100.000045      3.740485

CARBON   BALANCE     8.969221 LB AT/MOLN2.    96.64 PERCENT
HYDROGEN BALANCE    22.332065 LB AT/MOLN2.    96.24 PERCENT
OXYGEN BALANCE       0.475304 LB AT/MOLN2.    89.40 PERCENT

PERCENT O2 REACT     94.7847    PERCENT C4 REACT     15.4074

  CO      CO2    BUTEN   PARFIN   ALCOHL  ALDHYD   OXYGCO   WATER
          MOLE  PRODUCT PER MOLE  N-BUTANE
0.3478  0.0426  0.1540  0.3351   0.2058  0.0968   0.3353   0.4834
          MOLE  PRODUCT PER MOLE  N-BUTENES
2.2580  0.2768  1.0000  2.1750   1.3360  0.6284   2.1769   3.1376
          MOLE  PRODUCT PER MOLE  CO
1.0000  0.1225  0.4428  0.9632   0.5916  0.2783   0.9641   1.3895
          MOLE  PRODUCT PER MOLE  ETHENE
2.2987  0.2818  1.0180  2.2142   1.3600  0.6397   2.2161   3.1941
```

```
RUN NO =  62  SAMPLE NO =   5

  PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
     1        0.699618      0.025449      0.101932      0.069420
     2        0.443973      0.016150      0.064685      0.044053
     3       27.490211      1.000000      4.005247      2.727754
     4        3.178936      0.115638      0.463162      0.315434
     5        1.745298      0.063488      0.254285      0.173179
     6        1.298747      0.047244      0.189223      0.128870
     7        0.514927      0.018731      0.075023      0.051094
     8        0.221266      0.008048      0.032237      0.021955
     9        1.014454      0.036902      0.147803      0.100660
    10        0.145583      0.005295      0.021211      0.014445
    11        0.319212      0.011611      0.046508      0.031674
    12        1.335610      0.048584      0.194594      0.132527
    13       53.706428      1.953656      7.824874      5.329094
    14        0.032864      0.001195      0.004788      0.003261
    15        0.024192      0.000880      0.003524      0.002400
    16        0.308836      0.011234      0.044996      0.030644
    17        4.116934      0.149760      0.599825      0.408508
    18        0.324986      0.011821      0.047349      0.032247
    19        1.786697      0.064993      0.260316      0.177287
    20        0.444624      0.016173      0.064780      0.044118
    21        0.054961      0.001999      0.008007      0.005453
    22        0.282752      0.010285      0.041196      0.028056
    23        0.023972      0.000872      0.003492      0.002378
    24        0.117807      0.004285      0.017164      0.011689
    25        0.065162      0.002370      0.009493      0.006465
    26        0.019462      0.000707      0.002835      0.001931
    27        0.057244      0.002082      0.008340      0.005680
    28        0.020870      0.000759      0.003040      0.002070
    29        0.179416      0.006526      0.026140      0.017802
    30        0.025151      0.000914      0.003664      0.002495

  TOTALS     99.999969    100.000015      3.637661

CARBON   BALANCE     8.745096 LB AT/MOLN2.     94.22 PERCENT
HYDROGEN BALANCE    21.839576 LB AT/MOLN2.     94.12 PERCENT
OXYGEN BALANCE       0.443961 LB AT/MOLN2.     83.50 PERCENT

PERCENT O2 REACT     93.9244     PERCENT C4 REACT     15.8000

  CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.3154   0.0306   0.1642   0.3156   0.2024   0.0937   0.3376   0.4085
          MOLE PRODUCT PER MOLE N-BUTENES
1.9210   0.1866   1.0000   1.9223   1.2330   0.5708   2.0564   2.4878
          MOLE PRODUCT PER MOLE CO
1.0000   0.0971   0.5205   1.0006   0.6418   0.2971   1.0705   1.2950
          MOLE PRODUCT PER MOLE ETHENE
2.4476   0.2377   1.2741   2.4493   1.5711   0.7273   2.6203   3.1699
```

```
RUN NO =  63
REACTOR ENTRANCE CONDITIONS

AIR =    3.20 LB/HR               BUTANE =    9.40 LB/HR
TEMPERATURE =    702.00 DEG F
PRESSURE =  53.60 LB/SQ IN
OXYGEN = 8.5425 NITROGEN = 32.1361 BUTANE = 59.3213  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  1.8459  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   6.9442
DENSITY OF GAS MIXTURE =   0.1986 LB/CU FT
GAS VELOCITY =   8.26 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.16 SEC
REYNOLDS NUMBER =    6167
```

```
      RUN NO =   63   SAMPLE NO =   1

        PRD NO   MOL PERCENT    MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
           1        0.000000       0.000000      0.000000      0.000000
           2        7.657487       0.241292      9.836380     17.529582
           3       31.735332       1.000000     40.765434     72.648773
           4        0.081563       0.002570      0.104771      0.186715
           5        0.047136       0.001485      0.060549      0.107905
           6        0.022835       0.000719      0.029333      0.052275
           7        0.008318       0.000262      0.010685      0.019042
           8        0.004079       0.000128      0.005239      0.009337
           9        1.153166       0.036336      1.481292      2.639836
          10        0.157146       0.004951      0.201861      0.359740
          11        0.046847       0.001476      0.060177      0.107243
          12        0.054015       0.001702      0.069385      0.123652
          13       58.144531       1.832170     74.689208    133.104919
          14        0.000000       0.000000      0.000000      0.000000
          15        0.000000       0.000000      0.000000      0.000000
          16        0.070594       0.002224      0.090681      0.161605
          17        0.155665       0.004905      0.199958      0.356349
          18        0.148297       0.004672      0.190495      0.339484
          19        0.076758       0.002418      0.098599      0.175715
          20        0.053797       0.001695      0.069105      0.123153
          21        0.000000       0.000000      0.000000      0.000000
          22        0.361843       0.011401      0.464803      0.828334
          23        0.000000       0.000000      0.000000      0.000000
          24        0.020681       0.000651      0.026565      0.047343
          25        0.000000       0.000000      0.000000      0.000000
          26        0.000000       0.000000      0.000000      0.000000
          27        0.000000       0.000000      0.000000      0.000000
          28        0.000000       0.000000      0.000000      0.000000
          29        0.000000       0.000000      0.000000      0.000000
          30        0.000000       0.000000      0.000000      0.000000

        TOTALS     99.999984    099.999999      3.151062

  CARBON   BALANCE      7.514079 LB AT/MOLN2.    101.76 PERCENT
  HYDROGEN BALANCE     18.711200 LB AT/MOLN2.    101.36 PERCENT
  OXYGEN BALANCE        0.515348 LB AT/MOLN2.     96.93 PERCENT

  PERCENT O2 REACT       9.2281      PERCENT C4 REACT      0.7456

    CO       CO2    BUTEN   PARFIN  ALCOHL  ALDHYD   OXYGCO    WATER
             MOLE  PRODUCT PER MOLE N-BUTANE
  0.1867   0.1616   0.2308  0.1362  0.1757  0.5099   1.5140   0.3563
             MOLE  PRODUCT PER MOLE N-BUTENES
  0.8086   0.6999   1.0000  0.5902  0.7610  2.2087   6.5571   1.5433
             MOLE  PRODUCT PER MOLE CO
  1.0000   0.8655   1.2366  0.7299  0.9410  2.7313   8.1087   1.9085
             MOLE  PRODUCT PER MOLE ETHENE
  3.5717   3.0914   4.4169  2.6070  3.3613  9.7556  28.9626   6.8167
```

```
RUN NO =   63   SAMPLE NO =   2

 PRD NO   MOL  PERCENT   MOLS/MOL  N2   MOLS/MOXY R   MOLS/MBUT R
   1        0.030907       0.001000       0.009732      0.007530
   2        5.035277       0.163012       1.585565      1.226855
   3       30.888900       1.000000       9.726654      7.526143
   4        1.024332       0.033161       0.322553      0.249580
   5        0.570366       0.018465       0.179603      0.138970
   6        0.950611       0.030775       0.299339      0.231618
   7        0.132073       0.004275       0.041588      0.032180
   8        0.046799       0.001515       0.014736      0.011402
   9        1.502008       0.048626       0.472969      0.365967
  10        0.151369       0.004900       0.047664      0.036881
  11        0.410570       0.013291       0.129285      0.100036
  12        1.262007       0.040856       0.397395      0.307490
  13       52.914688       1.713064      16.662387     12.892768
  14        0.000000       0.000000       0.000000      0.000000
  15        0.000000       0.000000       0.000000      0.000000
  16        0.382507       0.012383       0.120448      0.093198
  17        2.169321       0.070229       0.683100      0.528559
  18        0.204170       0.006609       0.064291      0.049746
  19        1.179424       0.038182       0.371390      0.287369
  20        0.492821       0.015954       0.155185      0.120077
  21        0.064737       0.002095       0.020385      0.015773
  22        0.284624       0.009214       0.089625      0.069349
  23        0.022738       0.000736       0.007160      0.005540
  24        0.053777       0.001740       0.016934      0.013102
  25        0.059616       0.001930       0.018772      0.014525
  26        0.000000       0.000000       0.000000      0.000000
  27        0.000000       0.000000       0.000000      0.000000
  28        0.018055       0.000584       0.005685      0.004399
  29        0.148452       0.004806       0.046746      0.036170
  30        0.000000       0.000000       0.000000      0.000000

   TOTALS    099.999999     100.000061       3.237409

CARBON   BALANCE      7.507674 LB AT/MOLN2.    101.67 PERCENT
HYDROGEN BALANCE     18.641902 LB AT/MOLN2.    100.98 PERCENT
OXYGEN BALANCE        0.536037 LB AT/MOLN2.    100.82 PERCENT

PERCENT O2 REACT       38.6762     PERCENT C4 REACT       7.1979

   CO        CO2    BUTEN     PARFIN   ALCOHL    ALDHYD    OXYGCO    WATER
             MOLE  PRODUCT  PER MOLE  N-BUTANE
 0.2495    0.0931   0.4075    0.1900   0.3393    0.1829    0.6160    0.5285
             MOLE  PRODUCT  PER MOLE  N-BUTENES
 0.6124    0.2286   1.0000    0.4664   0.8326    0.4488    1.5116    1.2969
             MOLE  PRODUCT  PER MOLE  CO
 1.0000    0.3734   1.6328    0.7616   1.3595    0.7329    2.4683    2.1177
             MOLE  PRODUCT  PER MOLE  ETHENE
 1.0775    0.4023   1.7594    0.8206   1.4649    0.7897    2.6597    2.2820
```

```
  RUN NO =  63  SAMPLE NO =  3

    PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
       1        0.409390      0.013505      0.053660      0.038114
       2        0.428792      0.014145      0.056203      0.039920
       3       30.313938      1.000000      3.973336      2.822217
       4        2.998391      0.098911      0.393007      0.279149
       5        2.216689      0.073124      0.290547      0.206373
       6        2.498659      0.082426      0.327506      0.232624
       7        0.700159      0.023096      0.091771      0.065184
       8        0.117671      0.003881      0.015423      0.010955
       9        2.287084      0.075446      0.299774      0.212926
      10        0.101054      0.003333      0.013245      0.009408
      11        1.076277      0.035504      0.141070      0.100201
      12        1.286836      0.042450      0.168669      0.119804
      13       45.216384      1.491603      5.926642      4.209630
      14        0.073986      0.002440      0.009697      0.006888
      15        0.050362      0.001661      0.006601      0.004688
      16        0.601949      0.019857      0.078899      0.056041
      17        6.752976      0.222768      0.885132      0.628699
      18        0.136290      0.004495      0.017863      0.012688
      19        1.329945      0.043872      0.174319      0.123817
      20        0.504077      0.016628      0.066070      0.046929
      21        0.171196      0.005647      0.022439      0.015938
      22        0.262960      0.008674      0.034466      0.024481
      23        0.038985      0.001286      0.005109      0.003629
      24        0.060240      0.001987      0.007895      0.005608
      25        0.051108      0.001685      0.006698      0.004758
      26        0.041797      0.001378      0.005478      0.003891
      27        0.035997      0.001187      0.004718      0.003351
      28        0.021633      0.000713      0.002835      0.002014
      29        0.201306      0.006640      0.026385      0.018741
      30        0.014057      0.000463      0.001842      0.001308

    TOTALS     99.999954    100.000030      3.298814

CARBON   BALANCE     7.117500 LB AT/MOLN2.     96.39 PERCENT
HYDROGEN BALANCE    17.784534 LB AT/MOLN2.     96.34 PERCENT
OXYGEN BALANCE       0.484346 LB AT/MOLN2.     91.10 PERCENT

PERCENT O2 REACT     94.6787     PERCENT C4 REACT     19.1952

  CO       CO2    BUTEN   PARFIN  ALCOHL  ALDHYD  OXYGCO   WATER
         MOLE PRODUCT PER MOLE N-BUTANE
0.2791   0.0560  0.2200  0.3206  0.1623  0.0685  0.2671  0.6286
         MOLE PRODUCT PER MOLE N-BUTENES
1.2688   0.2547  1.0000  1.4573  0.7381  0.3117  1.2143  2.8576
         MOLE PRODUCT PER MOLE CO
1.0000   0.2007  0.7881  1.1485  0.5817  0.2456  0.9570  2.2521
         MOLE PRODUCT PER MOLE ETHENE
1.2000   0.2409  0.9457  1.3783  0.6980  0.2948  1.1484  2.7026
```

```
RUN NO =   63   SAMPLE NO =   4

 PRD NO   MOL  PERCENT    MOLS/MOL  N2    MOLS/MOXY R    MOLS/MBUT R
    1        0.820772       0.027179        0.107865       0.074891
    2        0.418099       0.013845        0.054946       0.038149
    3       30.198028       1.000000        3.968608       2.755437
    4        3.688765       0.122152        0.484775       0.336583
    5        2.366218       0.078356        0.310967       0.215907
    6        2.715235       0.089914        0.356834       0.247753
    7        0.734919       0.024336        0.096582       0.067058
    8        0.148252       0.004909        0.019483       0.013527
    9        2.518332       0.083393        0.330957       0.229786
   10        0.132450       0.004386        0.017406       0.012085
   11        0.672847       0.022281        0.088425       0.061394
   12        0.891458       0.029520        0.117155       0.081341
   13       44.784164       1.483016        5.885510       4.086357
   14        0.041831       0.001385        0.005497       0.003816
   15        0.038535       0.001276        0.005064       0.003516
   16        0.385989       0.012781        0.050726       0.035219
   17        6.867948       0.227430        0.902582       0.626670
   18        0.165227       0.005471        0.021714       0.015076
   19        1.172875       0.038839        0.154138       0.107019
   20        0.462955       0.015330        0.060841       0.042242
   21        0.102779       0.003403        0.013507       0.009378
   22        0.235195       0.007788        0.030909       0.021460
   23        0.025258       0.000836        0.003319       0.002304
   24        0.077663       0.002571        0.010206       0.007086
   25        0.069877       0.002313        0.009183       0.006376
   26        0.033238       0.001100        0.004368       0.003032
   27        0.023147       0.000766        0.003042       0.002112
   28        0.033048       0.001094        0.004343       0.003015
   29        0.159669       0.005287        0.020983       0.014569
   30        0.015399       0.000509        0.002023       0.001405

 TOTALS     99.999954     100.000030        3.311476

CARBON   BALANCE      7.026005 LB AT/MOLN2.     95.15 PERCENT
HYDROGEN BALANCE     17.585548 LB AT/MOLN2.     95.26 PERCENT
OXYGEN  BALANCE       0.488151 LB AT/MOLN2.     91.81 PERCENT

PERCENT O2 REACT      94.7915     PERCENT C4 REACT      19.6604

   CO        CO2     BUTEN     PARFIN    ALCOHL   ALDHYD    OXYGCO     WATER
             MOLE   PRODUCT   PER MOLE   N-BUTANE
 0.3365    0.0352    0.1427    0.3713    0.1339    0.0665    0.2350    0.6266
             MOLE   PRODUCT   PER MOLE   N-BUTENES
 2.3580    0.2467    1.0000    2.6018    0.9387    0.4660    1.6469    4.3904
             MOLE   PRODUCT   PER MOLE   CO
 1.0000    0.1046    0.4240    1.1033    0.3981    0.1976    0.6984    1.8618
             MOLE   PRODUCT   PER MOLE   ETHENE
 1.3585    0.1421    0.5761    1.4990    0.5408    0.2684    0.9488    2.5294
```

```
     RUN NO =  63   SAMPLE NO =   5

      PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
         1        0.666795       0.021975       0.087149       0.060515
         2        0.414724       0.013667       0.054203       0.037638
         3       30.343265       1.000000       3.965815       2.753847
         4        3.810564       0.125581       0.498034       0.345833
         5        2.446556       0.080629       0.319760       0.222040
         6        2.598112       0.085624       0.339568       0.235795
         7        0.786565       0.025922       0.102802       0.071385
         8        0.167878       0.005532       0.021941       0.015236
         9        1.682586       0.055451       0.219911       0.152705
        10        0.111528       0.003675       0.014576       0.010121
        11        0.886227       0.029206       0.115828       0.080430
        12        1.148003       0.037833       0.150042       0.104188
        13       44.993194       1.482806       5.880536       4.083421
        14        0.060375       0.001989       0.007890       0.005479
        15        0.049091       0.001617       0.006416       0.004455
        16        0.394046       0.012986       0.051501       0.035762
        17        6.537186       0.215441       0.854399       0.593291
        18        0.277729       0.009152       0.036298       0.025205
        19        1.274978       0.042018       0.166637       0.115712
        20        0.476697       0.015710       0.062303       0.043263
        21        0.089746       0.002957       0.011729       0.008145
        22        0.268981       0.008864       0.035155       0.024411
        23        0.029727       0.000979       0.003885       0.002697
        24        0.084243       0.002776       0.011010       0.007645
        25        0.079112       0.002607       0.010339       0.007179
        26        0.035286       0.001162       0.004611       0.003202
        27        0.022697       0.000748       0.002966       0.002059
        28        0.040110       0.001321       0.005242       0.003640
        29        0.202589       0.006676       0.026478       0.018386
        30        0.021600       0.000711       0.002823       0.001960

     TOTALS      99.999954     100.000030       3.295624

 CARBON    BALANCE      7.024767 LB AT/MOLN2.      95.13 PERCENT
 HYDROGEN BALANCE      17.559226 LB AT/MOLN2.      95.12 PERCENT
 OXYGEN BALANCE         0.490019 LB AT/MOLN2.      92.17 PERCENT

 PERCENT O2 REACT       94.8583      PERCENT C4 REACT       19.6717

   CO          CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
              MOLE PRODUCT PER MOLE N-BUTANE
 0.3458     0.0357   0.1846   0.3691   0.1454   0.0781   0.2635   0.5932
              MOLE PRODUCT PER MOLE N-BUTENES
 1.8732     0.1937   1.0000   1.9996   0.7878   0.4234   1.4273   3.2135
              MOLE PRODUCT PER MOLE CO
 1.0000     0.1034   0.5338   1.0675   0.4205   0.2260   0.7619   1.7155
              MOLE PRODUCT PER MOLE ETHENE
 1.4666     0.1516   0.7829   1.5656   0.6168   0.3315   1.1175   2.5161
```

```
RUN NO =  64
REACTOR ENTRANCE CONDITIONS


AIR =    2.50 LB/HR              BUTANE =    8.20 LB/HR
TEMPERATURE =    692.00 DEG F
PRESSURE =  53.58 LB/SQ IN
OXYGEN = 7.9898 NITROGEN = 30.0572 BUTANE = 61.9528  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.0611  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   7.7538
DENSITY OF GAS MIXTURE =   0.2036 LB/CU FT
GAS VELOCITY =   6.84 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.41 SEC
REYNOLDS NUMBER =    5370
```

```
RUN NO =  64   SAMPLE NO =  1

PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
   1       0.000000       0.000000       0.000000       0.000000
   2       6.970619       0.234989       7.621179      33.067695
   3      29.663585       1.000000      32.432060     140.720153
   4       0.021427       0.000722       0.023427       0.101649
   5       0.004032       0.000135       0.004408       0.019127
   6       0.029030       0.000978       0.031740       0.137718
   7       0.002504       0.000084       0.002738       0.011881
   8       0.004466       0.000150       0.004883       0.021187
   9       0.967696       0.032622       1.058010       4.590621
  10       0.144446       0.004869       0.157927       0.685234
  11       0.007480       0.000252       0.008178       0.035485
  12       0.027343       0.000921       0.029894       0.129711
  13      60.930694       2.054057      66.617294     289.047119
  14       0.010948       0.000369       0.011970       0.051939
  15       0.000000       0.000000       0.000000       0.000000
  16       0.636260       0.021449       0.695641       3.018333
  17       0.028656       0.000966       0.031330       0.135941
  18       0.098604       0.003324       0.107807       0.467768
  19       0.012299       0.000414       0.013446       0.058345
  20       0.049133       0.001656       0.053719       0.233083
  21       0.000000       0.000000       0.000000       0.000000
  22       0.285185       0.009614       0.311801       1.352883
  23       0.000000       0.000000       0.000000       0.000000
  24       0.060674       0.002045       0.066337       0.287831
  25       0.044997       0.001516       0.049197       0.213463
  26       0.000000       0.000000       0.000000       0.000000
  27       0.000000       0.000000       0.000000       0.000000
  28       0.000000       0.000000       0.000000       0.000000
  29       0.000000       0.000000       0.000000       0.000000
  30       0.000000       0.000000       0.000000       0.000000

TOTALS    99.999984      99.999984       3.371137

CARBON   BALANCE     8.401590 LB AT/MOLN2.    101.90 PERCENT
HYDROGEN BALANCE    20.880924 LB AT/MOLN2.    101.30 PERCENT
OXYGEN BALANCE       0.533136 LB AT/MOLN2.    100.28 PERCENT

PERCENT O2 REACT     11.5993     PERCENT C4 REACT      0.3447

   CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.1016   3.0183   0.1651   0.0521   0.0583   0.9886   2.6133   0.1359
           MOLE  PRODUCT  PER MOLE  N-BUTENES
0.6153  18.2710   1.0000   0.3159   0.3531   5.9848  15.8197   0.8229
           MOLE  PRODUCT  PER MOLE  CO
1.0000  29.6935   1.6251   0.5134   0.5739   9.7264  25.7096   1.3373
           MOLE  PRODUCT  PER MOLE  ETHENE
0.7380  21.9166   1.1995   0.3790   0.4236   7.1790  18.9762   0.9870
```

```
     RUN NO =   64   SAMPLE NO =   2

      PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
         1       0.000000      0.000000      0.000000      0.000000
         2       6.202250      0.209448      3.715347      2.714990
         3      29.612247      1.000000     17.738689     12.962547
         4       0.221516      0.007480      0.132695      0.096967
         5       0.156373      0.005280      0.093672      0.068451
         6       0.063684      0.002150      0.038148      0.027877
         7       0.015429      0.000521      0.009242      0.006754
         8       0.027751      0.000937      0.016623      0.012147
         9       2.517343      0.085010      1.507969      1.101948
        10       0.150590      0.005085      0.090208      0.065919
        11       0.155970      0.005267      0.093431      0.068275
        12       0.095724      0.003232      0.057341      0.041902
        13      58.751220      1.984017     35.193870     25.717922
        14       0.062549      0.002112      0.037469      0.027380
        15       0.000000      0.000000      0.000000      0.000000
        16       1.172799      0.039605      0.702544      0.513384
        17       0.122429      0.004134      0.073339      0.053592
        18       0.031309      0.001057      0.018755      0.013705
        19       0.115934      0.003915      0.069448      0.050749
        20       0.092113      0.003110      0.055178      0.040321
        21       0.016359      0.000552      0.009800      0.007161
        22       0.309779      0.010461      0.185567      0.135603
        23       0.000000      0.000000      0.000000      0.000000
        24       0.070367      0.002376      0.042152      0.030803
        25       0.000000      0.000000      0.000000      0.000000
        26       0.000000      0.000000      0.000000      0.000000
        27       0.000000      0.000000      0.000000      0.000000
        28       0.036373      0.001228      0.021789      0.015922
        29       0.000000      0.000000      0.000000      0.000000
        30       0.000000      0.000000      0.000000      0.000000

     TOTALS     99.999969    099.999999      3.376981

CARBON   BALANCE      8.360897 LB AT/MOLN2.    101.40 PERCENT
HYDROGEN BALANCE     20.641960 LB AT/MOLN2.    100.14 PERCENT
OXYGEN BALANCE        0.532423 LB AT/MOLN2.    100.14 PERCENT

PERCENT O2 REACT     21.2073     PERCENT C4 REACT      3.7428

   CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.0969   0.5133   0.1101   0.0873   0.0579   0.0848   0.2942   0.0535
            MOLE  PRODUCT  PER MOLE  N-BUTENES
0.8800   4.6596   1.0000   0.7928   0.5256   0.7699   2.6708   0.4864
            MOLE  PRODUCT  PER MOLE  CO
1.0000   5.2944   1.1362   0.9008   0.5972   0.8748   3.0347   0.5526
            MOLE  PRODUCT  PER MOLE  ETHENE
3.4783  18.4158   3.9522   3.1334   2.0773   3.0429  10.5557   1.9224
```

```
RUN NO =  64   SAMPLE NO =  3

  PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
     1        0.573815      0.019986      0.080352      0.065248
     2        0.490452      0.017083      0.068678      0.055769
     3       28.709751      1.000000      4.020269      3.264598
     4        2.471805      0.086096      0.346130      0.281070
     5        1.527088      0.053190      0.213840      0.173645
     6        1.882644      0.065575      0.263629      0.214076
     7        0.420999      0.014664      0.058953      0.047872
     8        0.073687      0.002566      0.010318      0.008379
     9        3.047624      0.106152      0.426763      0.346546
    10        0.096536      0.003362      0.013518      0.010977
    11        0.992995      0.034587      0.139050      0.112913
    12        0.973959      0.033924      0.136384      0.110749
    13       50.381210      1.754846      7.054955      5.728870
    14        0.037751      0.001314      0.005286      0.004292
    15        0.030897      0.001076      0.004326      0.003513
    16        0.901998      0.031417      0.126308      0.102566
    17        4.566679      0.159063      0.639478      0.519279
    18        0.233911      0.008147      0.032754      0.026598
    19        1.488973      0.051863      0.208503      0.169311
    20        0.332118      0.011568      0.046507      0.037765
    21        0.105674      0.003680      0.014797      0.012016
    22        0.217728      0.007583      0.030488      0.024758
    23        0.042113      0.001466      0.005897      0.004788
    24        0.061566      0.002144      0.008621      0.007000
    25        0.047189      0.001643      0.006607      0.005365
    26        0.021707      0.000756      0.003039      0.002468
    27        0.020133      0.000701      0.002819      0.002289
    28        0.037451      0.001304      0.005244      0.004258
    29        0.191276      0.006662      0.026784      0.021750
    30        0.020474      0.000713      0.002867      0.002328

 TOTALS      99.999969    100.000030      3.483139

CARBON   BALANCE      8.138820 LB AT/MOLN2.     98.71 PERCENT
HYDROGEN BALANCE     20.190696 LB AT/MOLN2.     97.95 PERCENT
OXYGEN BALANCE        0.440397 LB AT/MOLN2.     82.83 PERCENT

PERCENT O2 REACT      93.5734     PERCENT C4 REACT      14.8613

   CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2810   0.1025   0.2236   0.2951   0.2055   0.0736   0.3206   0.5192
           MOLE  PRODUCT  PER MOLE  N-BUTENES
1.2566   0.4585   1.0000   1.3195   0.9190   0.3293   1.4338   2.3217
           MOLE  PRODUCT  PER MOLE  CO
1.0000   0.3649   0.7957   1.0500   0.7313   0.2620   1.1409   1.8475
           MOLE  PRODUCT  PER MOLE  ETHENE
1.3129   0.4791   1.0447   1.3786   0.9601   0.3440   1.4980   2.4256
```

```
RUN NO =   64   SAMPLE NO =   4
 PRD NO   MOL PERCENT   MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
   1        0.860754      0.029921       0.118408       0.084431
   2        0.377567      0.013125       0.051939       0.037035
   3       28.767009      1.000000       3.957296       2.821745
   4        2.955873      0.102752       0.406620       0.289940
   5        2.227372      0.077428       0.306405       0.218482
   6        2.161430      0.075135       0.297334       0.212013
   7        0.687290      0.023891       0.094546       0.067416
   8        0.111819      0.003887       0.015382       0.010968
   9        1.349076      0.046896       0.185584       0.132330
  10        0.109867      0.003819       0.015113       0.010776
  11        0.733587      0.025500       0.100914       0.071957
  12        0.886041      0.030800       0.121887       0.086911
  13       49.098739      1.706772       6.754204       4.816077
  14        0.053925      0.001874       0.007418       0.005289
  15        0.048008      0.001668       0.006604       0.004709
  16        0.572718      0.019908       0.078785       0.056177
  17        6.390933      0.222161       0.879160       0.626884
  18        0.244768      0.008508       0.033671       0.024009
  19        1.013994      0.035248       0.139488       0.099462
  20        0.470619      0.016359       0.064740       0.046162
  21        0.109912      0.003820       0.015119       0.010781
  22        0.265836      0.009241       0.036569       0.026075
  23        0.043620      0.001516       0.006000       0.004278
  24        0.104554      0.003634       0.014382       0.010255
  25        0.056197      0.001953       0.007730       0.005512
  26        0.032100      0.001115       0.004415       0.003148
  27        0.040608      0.001411       0.005586       0.003983
  28        0.028133      0.000977       0.003870       0.002759
  29        0.181558      0.006311       0.024975       0.017808
  30        0.016276      0.000565       0.002239       0.001596

   TOTALS    099.999999     100.000045      3.476204

CARBON   BALANCE      7.800337 LB AT/MOLN2.      94.61 PERCENT
HYDROGEN BALANCE     19.592727 LB AT/MOLN2.      95.05 PERCENT
OXYGEN BALANCE        0.481647 LB AT/MOLN2.      90.59 PERCENT

PERCENT O2 REACT      95.0624     PERCENT C4 REACT      17.1937

   CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE PRODUCT PER MOLE N-BUTANE
 0.2899   0.0561   0.1588   0.3812   0.1312   0.0844   0.2558   0.6268
            MOLE PRODUCT PER MOLE N-BUTENES
 1.8250   0.3536   1.0000   2.4000   0.8258   0.5313   1.6103   3.9459
            MOLE PRODUCT PER MOLE CO
 1.0000   0.1937   0.5479   1.3150   0.4525   0.2911   0.8823   2.1621
            MOLE PRODUCT PER MOLE ETHENE
 1.3675   0.2649   0.7493   1.7984   0.6188   0.3981   1.2066   2.9568
```

```
RUN NO =  64   SAMPLE NO =   5

 PRD NO   MOL PERCENT    MOLS/MOL N2   MOLS/MOXY R    MOLS/MBUT R
    1       0.867718       0.031067      0.122950       0.086365
    2       0.367024       0.013140      0.052004       0.036530
    3      27.930305       1.000000      3.957543       2.779954
    4       3.194267       0.114365      0.452606       0.317931
    5       2.328342       0.083362      0.329911       0.231744
    6       2.261506       0.080969      0.320440       0.225091
    7       0.862370       0.030875      0.122192       0.085833
    8       0.116660       0.004176      0.016529       0.011611
    9       2.619298       0.093779      0.371137       0.260703
   10       0.112747       0.004036      0.015975       0.011221
   11       0.625527       0.022396      0.088633       0.062259
   12       1.037733       0.037154      0.147040       0.103287
   13      47.521881       1.701445      6.733541       4.729940
   14       0.055552       0.001988      0.007871       0.005529
   15       0.048552       0.001738      0.006879       0.004832
   16       0.335033       0.011995      0.047472       0.033346
   17       6.826504       0.244412      0.967271       0.679454
   18       0.247902       0.008875      0.035126       0.024674
   19       1.503299       0.053823      0.213007       0.149626
   20       0.331213       0.011858      0.046930       0.032966
   21       0.096240       0.003445      0.013636       0.009579
   22       0.195577       0.007002      0.027712       0.019466
   23       0.033438       0.001197      0.004737       0.003328
   24       0.064454       0.002307      0.009132       0.006415
   25       0.071016       0.002542      0.010062       0.007068
   26       0.031560       0.001129      0.004471       0.003141
   27       0.029982       0.001073      0.004248       0.002984
   28       0.028933       0.001035      0.004099       0.002879
   29       0.216701       0.007758      0.030705       0.021568
   30       0.038854       0.001391      0.005505       0.003867

  TOTALS   100.000030    100.000045      3.580343

CARBON   BALANCE      7.981754 LB AT/MOLN2.      96.81 PERCENT
HYDROGEN BALANCE     20.051712 LB AT/MOLN2.      97.28 PERCENT
OXYGEN BALANCE        0.512491 LB AT/MOLN2.      96.39 PERCENT

PERCENT O2 REACT      95.0565     PERCENT C4 REACT      17.4521

  CO       CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.3179   0.0333   0.1655   0.4155   0.1839   0.0670   0.2875   0.6794
          MOLE  PRODUCT  PER MOLE  N-BUTENES
1.9204   0.2014   1.0000   2.5101   1.1109   0.4049   1.7370   4.1042
          MOLE  PRODUCT  PER MOLE  CO
1.0000   0.1048   0.5207   1.3070   0.5784   0.2108   0.9044   2.1371
          MOLE  PRODUCT  PER MOLE  ETHENE
1.4124   0.1481   0.7354   1.8461   0.8170   0.2978   1.2775   3.0185
```

```
RUN NO =  65
REACTOR ENTRANCE CONDITIONS


AIR =    2.95 LB/HR               BUTANE =    9.20 LB/HR
TEMPERATURE =    687.00 DEG F
PRESSURE =  53.47 LB/SQ IN
OXYGEN = 8.2410 NITROGEN = 31.0020 BUTANE = 60.7568  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  1.9597  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   7.3724
DENSITY OF GAS MIXTURE =   0.2026 LB/CU FT
GAS VELOCITY =   7.81 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.23 SEC
REYNOLDS NUMBER =    6072
```

```
      RUN NO =   65   SAMPLE NO =   1

       PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
         1        0.000000       0.000000       0.000000       0.000000
         2        7.199123       0.234868       7.587571      16.622116
         3       30.651729       1.000000      32.305625      70.772033
         4        0.058561       0.001910       0.061721       0.135213
         5        0.054990       0.001794       0.057958       0.126968
         6        0.028495       0.000929       0.030032       0.065792
         7        0.001882       0.000061       0.001983       0.004345
         8        0.003691       0.000120       0.003890       0.008523
         9        0.990311       0.032308       1.043746       2.286538
        10        0.149536       0.004878       0.157604       0.345265
        11        0.026498       0.000864       0.027928       0.061182
        12        0.132536       0.004323       0.139687       0.306013
        13       59.637145       1.945637      62.855026     137.696685
        14        0.000000       0.000000       0.000000       0.000000
        15        0.000000       0.000000       0.000000       0.000000
        16        0.082486       0.002691       0.086937       0.190453
        17        0.148426       0.004842       0.156435       0.342704
        18        0.273058       0.008908       0.287791       0.630465
        19        0.100812       0.003288       0.106252       0.232767
        20        0.045209       0.001474       0.047649       0.104385
        21        0.025941       0.000846       0.027341       0.059896
        22        0.347589       0.011339       0.366344       0.802551
        23        0.000000       0.000000       0.000000       0.000000
        24        0.042068       0.001372       0.044337       0.097131
        25        0.000000       0.000000       0.000000       0.000000
        26        0.000000       0.000000       0.000000       0.000000
        27        0.000000       0.000000       0.000000       0.000000
        28        0.000000       0.000000       0.000000       0.000000
        29        0.000000       0.000000       0.000000       0.000000
        30        0.000000       0.000000       0.000000       0.000000

      TOTALS    099.999999      99.999969       3.262459

 CARBON    BALANCE       7.972114 LB AT/MOLN2.    101.69 PERCENT
 HYDROGEN BALANCE       19.857952 LB AT/MOLN2.    101.32 PERCENT
 OXYGEN BALANCE          0.509102 LB AT/MOLN2.     95.75 PERCENT

 PERCENT O2 REACT      11.6447     PERCENT C4 REACT       0.7209

    CO        CO2     BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
              MOLE  PRODUCT  PER MOLE  N-BUTANE
 0.1352    0.1904    0.3671    0.1398   0.2926   0.8319   1.9271   0.3427
              MOLE  PRODUCT  PER MOLE  N-BUTENES
 0.3682    0.5186    1.0000    0.3808   0.7970   2.2657   5.2484   0.9332
              MOLE  PRODUCT  PER MOLE  CO
 1.0000    1.4085    2.7156    1.0342   2.1644   6.1531  14.2530   2.5345
              MOLE  PRODUCT  PER MOLE  ETHENE
 2.0551    2.8947    5.5810    2.1254   4.4482  12.6454  29.2918   5.2088
```

```
   RUN NO =   65   SAMPLE NO =   2

     PRD NO    MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
        1         0.000000       0.000000       0.000000       0.000000
        2         5.869879       0.192478       2.624301       3.078124
        3        30.496330       1.000000      13.634277      15.992071
        4         0.311511       0.010214       0.139270       0.163354
        5         0.116816       0.003830       0.052226       0.061258
        6         0.122901       0.004030       0.054946       0.064448
        7         0.016033       0.000525       0.007168       0.008407
        8         0.010783       0.000353       0.004820       0.005654
        9         1.288694       0.042257       0.576148       0.675782
       10         0.134624       0.004414       0.060187       0.070596
       11         0.387000       0.012690       0.173020       0.202940
       12         0.351809       0.011536       0.157286       0.184486
       13        57.858734       1.897236      25.867439      30.340728
       14         0.000000       0.000000       0.000000       0.000000
       15         0.000000       0.000000       0.000000       0.000000
       16         0.127525       0.004181       0.057013       0.066873
       17         0.576548       0.018905       0.257762       0.302337
       18         0.188316       0.006175       0.084192       0.098752
       19         1.453767       0.047670       0.649949       0.762345
       20         0.132053       0.004330       0.059038       0.069248
       21         0.022551       0.000739       0.010082       0.011825
       22         0.275722       0.009041       0.123269       0.144586
       23         0.000000       0.000000       0.000000       0.000000
       24         0.059868       0.001963       0.026766       0.031394
       25         0.053443       0.001752       0.023893       0.028025
       26         0.000000       0.000000       0.000000       0.000000
       27         0.000000       0.000000       0.000000       0.000000
       28         0.024833       0.000814       0.011102       0.013022
       29         0.120429       0.003948       0.053841       0.063152
       30         0.000000       0.000000       0.000000       0.000000

     TOTALS      99.999923     100.000045       3.279085

CARBON    BALANCE     7.971753 LB AT/MOLN2.    101.69 PERCENT
HYDROGEN BALANCE    19.870773 LB AT/MOLN2.    101.39 PERCENT
OXYGEN BALANCE       0.498874 LB AT/MOLN2.     93.83 PERCENT

PERCENT O2 REACT    27.5915     PERCENT C4 REACT      3.1907

  CO        CO2   BUTEN    PARFIN   ALCOHL  ALDHYD  OXYGCO   WATER
            MOLE PRODUCT PER MOLE N-BUTANE
0.1633   0.0668  0.3874  0.0753  0.8373  0.1993  1.2223  0.3023
            MOLE PRODUCT PER MOLE N-BUTENES
0.4216   0.1726  1.0000  0.1944  2.1612  0.5146  3.1550  0.7803
            MOLE PRODUCT PER MOLE CO
1.0000   0.4093  2.3716  0.4610  5.1258  1.2206  7.4828  1.8508
            MOLE PRODUCT PER MOLE ETHENE
2.5346   1.0376  6.0114  1.1686 12.9921  3.0938 18.9663  4.6911
```

```
RUN NO =  65  SAMPLE NO =  3
PRD NO  MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
   1      0.645106      0.021176      0.083430      0.065751
   2      0.365560      0.012000      0.047277      0.037259
   3     30.463356      1.000000      3.939757      3.104948
   4      2.088984      0.068573      0.270163      0.212917
   5      1.535403      0.050401      0.198570      0.156494
   6      1.618265      0.053121      0.209286      0.164940
   7      0.439259      0.014419      0.056808      0.044771
   8      0.130481      0.004283      0.016874      0.013299
   9      1.290527      0.042363      0.166901      0.131535
  10      0.111633      0.003664      0.014437      0.011378
  11      0.513146      0.016844      0.066364      0.052301
  12      1.295655      0.042531      0.167564      0.132058
  13     49.889854      1.637700      6.452141      5.084975
  14      0.034760      0.001141      0.004495      0.003542
  15      0.034816      0.001142      0.004502      0.003548
  16      0.422845      0.013880      0.054685      0.043098
  17      5.320844      0.174663      0.688132      0.542322
  18      0.146228      0.004800      0.018911      0.014904
  19      2.141420      0.070294      0.276945      0.218262
  20      0.546768      0.017948      0.070712      0.055728
  21      0.067901      0.002228      0.008781      0.006920
  22      0.307080      0.010080      0.039714      0.031298
  23      0.049105      0.001611      0.006350      0.005005
  24      0.119322      0.003916      0.015431      0.012161
  25      0.071067      0.002332      0.009190      0.007243
  26      0.041001      0.001345      0.005302      0.004179
  27      0.039216      0.001287      0.005071      0.003997
  28      0.039790      0.001306      0.005145      0.004055
  29      0.210503      0.006910      0.027223      0.021455
  30      0.020302      0.000666      0.002625      0.002069

  TOTALS     99.999984   100.000061      3.282633

CARBON   BALANCE     7.427664 LB AT/MOLN2.    94.75 PERCENT
HYDROGEN BALANCE    18.671127 LB AT/MOLN2.    95.27 PERCENT
OXYGEN BALANCE       0.419728 LB AT/MOLN2.    78.94 PERCENT

PERCENT O2 REACT      95.4857    PERCENT C4 REACT     16.4339

   CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
          MOLE PRODUCT PER MOLE N-BUTANE
 0.2129   0.0430   0.1843   0.2803   0.2508   0.0867   0.3872   0.5423
          MOLE PRODUCT PER MOLE N-BUTENES
 1.1548   0.2337   1.0000   1.5204   1.3604   0.4707   2.1006   2.9416
          MOLE PRODUCT PER MOLE CO
 1.0000   0.2024   0.8658   1.3165   1.1780   0.4076   1.8189   2.5470
          MOLE PRODUCT PER MOLE ETHENE
 1.2908   0.2612   1.1177   1.6995   1.5206   0.5262   2.3480   3.2879
```

```
     RUN NO =   65   SAMPLE NO =   4

       PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
          1        0.812555      0.026985      0.106675      0.076763
          2        0.386904      0.012849      0.050794      0.036551
          3       30.110332      1.000000      3.952988      2.844575
          4        2.466875      0.081927      0.323859      0.233049
          5        2.234274      0.074202      0.293323      0.211075
          6        1.776444      0.058997      0.233217      0.167823
          7        0.763129      0.025344      0.100186      0.072094
          8        0.125014      0.004151      0.016412      0.011810
          9        0.947249      0.031459      0.124358      0.089488
         10        0.127287      0.004227      0.016710      0.012025
         11        0.379138      0.012591      0.049774      0.035817
         12        1.163611      0.038644      0.152762      0.109928
         13       48.424064      1.608220      6.357276      4.574705
         14        0.053353      0.001771      0.007004      0.005040
         15        0.188701      0.006266      0.024773      0.017826
         16        0.464381      0.015422      0.060965      0.043870
         17        6.197464      0.205825      0.813624      0.585485
         18        0.140305      0.004659      0.018419      0.013254
         19        1.904916      0.063264      0.250083      0.179960
         20        0.437568      0.014532      0.057445      0.041337
         21        0.072098      0.002394      0.009465      0.006811
         22        0.291376      0.009676      0.038252      0.027526
         23        0.035655      0.001184      0.004681      0.003368
         24        0.111156      0.003691      0.014593      0.010501
         25        0.071426      0.002372      0.009377      0.006747
         26        0.019376      0.000643      0.002543      0.001830
         27        0.023961      0.000795      0.003145      0.002263
         28        0.046800      0.001554      0.006144      0.004421
         29        0.196913      0.006539      0.025851      0.018602
         30        0.027876      0.000925      0.003659      0.002633

       TOTALS     99.999984    100.000015      3.321120

 CARBON    BALANCE      7.327700 LB AT/MOLN2.     93.47 PERCENT
 HYDROGEN BALANCE      18.522842 LB AT/MOLN2.     94.51 PERCENT
 OXYGEN BALANCE         0.456532 LB AT/MOLN2.     85.87 PERCENT

 PERCENT O2 REACT      95.1661      PERCENT C4 REACT     17.9381

   CO         CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
              MOLE PRODUCT PER MOLE N-BUTANE
 0.2330   0.0438   0.1457   0.3717   0.2072   0.0673   0.3192   0.5854
              MOLE PRODUCT PER MOLE N-BUTENES
 1.5990   0.3010   1.0000   2.5506   1.4216   0.4621   2.1905   4.0171
              MOLE PRODUCT PER MOLE CO
 1.0000   0.1882   0.6253   1.5951   0.8891   0.2890   1.3699   2.5122
              MOLE PRODUCT PER MOLE ETHENE
 1.3886   0.2614   0.8684   2.2150   1.2346   0.4013   1.9023   3.4886
```

```
   RUN NO =  65  SAMPLE NO =  5

    PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
       1       0.895310      0.029480      0.115889      0.082206
       2       0.347419      0.011439      0.044970      0.031899
       3      30.369655      1.000000      3.931080      2.788519
       4       2.460268      0.081010      0.318459      0.225900
       5       2.196832      0.072336      0.284360      0.201711
       6       1.828020      0.060192      0.236620      0.167847
       7       0.710834      0.023406      0.092011      0.065268
       8       0.150978      0.004971      0.019542      0.013862
       9       0.930045      0.030624      0.120386      0.085396
      10       0.057163      0.001882      0.007399      0.005248
      11       0.255698      0.008419      0.033097      0.023478
      12       1.506942      0.049620      0.195060      0.138366
      13      48.626487      1.601153      6.294262      4.464848
      14       0.032371      0.001065      0.004190      0.002972
      15       0.019792      0.000651      0.002561      0.001817
      16       0.346361      0.011404      0.044833      0.031802
      17       5.996156      0.197439      0.776148      0.550562
      18       0.211997      0.006980      0.027441      0.019465
      19       1.864790      0.061403      0.241380      0.171223
      20       0.344688      0.011349      0.044616      0.031649
      21       0.030832      0.001015      0.003990      0.002830
      22       0.305613      0.010063      0.039558      0.028061
      23       0.028192      0.000928      0.003649      0.002588
      24       0.091497      0.003012      0.011843      0.008401
      25       0.067468      0.002221      0.008733      0.006194
      26       0.028326      0.000932      0.003666      0.002600
      27       0.034481      0.001135      0.004463      0.003166
      28       0.034361      0.001131      0.004447      0.003155
      29       0.192874      0.006350      0.024965      0.017709
      30       0.034731      0.001143      0.004495      0.003189

    TOTALS    99.999954    100.000030      3.292761

CARBON   BALANCE     7.267541 LB AT/MOLN2.     92.70 PERCENT
HYDROGEN BALANCE    18.356693 LB AT/MOLN2.     93.66 PERCENT
OXYGEN BALANCE       0.431806 LB AT/MOLN2.     81.22 PERCENT

PERCENT O2 REACT     95.6965     PERCENT C4 REACT     18.2987

  CO       CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.2259  0.0318  0.1618  0.3630  0.1943  0.0626  0.3002  0.5505
          MOLE PRODUCT PER MOLE N-BUTENES
1.3957  0.1965  1.0000  2.2431  1.2009  0.3872  1.8550  3.4018
          MOLE PRODUCT PER MOLE CO
1.0000  0.1407  0.7164  1.6071  0.8604  0.2774  1.3290  2.4371
          MOLE PRODUCT PER MOLE ETHENE
1.3458  0.1894  0.9642  2.1629  1.1579  0.3734  1.7887  3.2801
```

```
RUN NO =  66
REACTOR ENTRANCE CONDITIONS


AIR =   2.85 LB/HR            BUTANE =   9.40 LB/HR
TEMPERATURE =   708.00 DEG F
PRESSURE =  53.40 LB/SQ IN
OXYGEN = 7.9624 NITROGEN = 29.9540 BUTANE = 62.0835  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.0726  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   7.7970
DENSITY OF GAS MIXTURE =  0.2003 LB/CU FT
GAS VELOCITY =   7.97 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.21 SEC
REYNOLDS NUMBER =    6080
```

```
RUN NO =  66  SAMPLE NO =  1

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
     1       0.000000       0.000000       0.000000       0.000000
     2       6.576795       0.224218       5.389362       5.733351
     3      29.332046       1.000000      24.036178      25.570350
     4       0.097794       0.003334       0.080137       0.085252
     5       0.136555       0.004655       0.111900       0.119042
     6       0.079419       0.002707       0.065080       0.069234
     7       0.024160       0.000823       0.019798       0.021062
     8       0.009873       0.000336       0.008090       0.008607
     9       1.996633       0.068070       1.636143       1.740574
    10       0.124050       0.004229       0.101653       0.108141
    11       0.357504       0.012188       0.292957       0.311655
    12       0.132832       0.004528       0.108849       0.115797
    13      59.647338       2.033521      48.878082      51.997848
    14       0.000000       0.000000       0.000000       0.000000
    15       0.000000       0.000000       0.000000       0.000000
    16       0.179830       0.006130       0.147362       0.156768
    17       0.275342       0.009387       0.225629       0.240030
    18       0.145173       0.004949       0.118962       0.126556
    19       0.348926       0.011895       0.285928       0.304178
    20       0.076268       0.002600       0.062498       0.066487
    21       0.045593       0.001554       0.037361       0.039746
    22       0.303899       0.010360       0.249030       0.264925
    23       0.000000       0.000000       0.000000       0.000000
    24       0.073162       0.002494       0.059952       0.063779
    25       0.036902       0.001258       0.030239       0.032169
    26       0.000000       0.000000       0.000000       0.000000
    27       0.000000       0.000000       0.000000       0.000000
    28       0.000000       0.000000       0.000000       0.000000
    29       0.000000       0.000000       0.000000       0.000000
    30       0.000000       0.000000       0.000000       0.000000

 TOTALS    099.999999     100.000015       3.409240

CARBON   BALANCE      8.501394 LB AT/MOLN2.    102.54 PERCENT
HYDROGEN BALANCE     21.116664 LB AT/MOLN2.    101.88 PERCENT
OXYGEN BALANCE        0.508532 LB AT/MOLN2.     95.65 PERCENT

PERCENT O2 REACT     15.6510     PERCENT C4 REACT      1.8868

  CO       CO2    BUTEN   PARFIN  ALCOHL  ALDHYD   OXYGCO    WATER
           MOLE PRODUCT PER MOLE N-BUTANE
0.0852   0.1567   0.4274  0.1487  0.3439  0.2568   0.8978   0.2400
           MOLE PRODUCT PER MOLE N-BUTENES
0.1994   0.3667   1.0000  0.3479  0.8045  0.6008   2.1004   0.5615
           MOLE PRODUCT PER MOLE CO
1.0000   1.8388   5.0139  1.7443  4.0341  3.0124  10.5315   2.8155
           MOLE PRODUCT PER MOLE ETHENE
1.2313   2.2643   6.1739  2.1479  4.9675  3.7094  12.9681   3.4669
```

```
   RUN NO =  66   SAMPLE NO =  2

     PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
        1        0.292503      0.010588      0.062348      0.057334
        2        2.652030      0.095999      0.565295      0.519834
        3       27.625328      1.000000      5.888493      5.414947
        4        1.949549      0.070571      0.415557      0.382138
        5        1.323973      0.047926      0.282212      0.259517
        6        1.832028      0.066316      0.390507      0.359102
        7        0.280251      0.010144      0.059737      0.054933
        8        0.048450      0.001753      0.010327      0.009496
        9        2.153348      0.077948      0.458998      0.422086
       10        0.110785      0.004010      0.023614      0.021715
       11        0.471870      0.017081      0.100581      0.092493
       12        1.218301      0.044100      0.259687      0.238803
       13       52.155380      1.887955     11.117212     10.223176
       14        0.027397      0.000991      0.005839      0.005370
       15        0.018168      0.000657      0.003872      0.003561
       16        0.479456      0.017355      0.102198      0.093980
       17        3.860398      0.139741      0.822865      0.756691
       18        0.236508      0.008561      0.050413      0.046358
       19        1.806731      0.065401      0.385114      0.354144
       20        0.599046      0.021684      0.127690      0.117421
       21        0.087453      0.003165      0.018641      0.017142
       22        0.311721      0.011283      0.066445      0.061101
       23        0.044717      0.001618      0.009531      0.008765
       24        0.096143      0.003480      0.020493      0.018845
       25        0.075703      0.002740      0.016136      0.014838
       26        0.017246      0.000624      0.003676      0.003380
       27        0.012858      0.000465      0.002740      0.002520
       28        0.029182      0.001056      0.006220      0.005720
       29        0.183618      0.006646      0.039139      0.035991
       30        0.000000      0.000000      0.000000      0.000000

     TOTALS     99.999954     99.999984      3.619867

 CARBON   BALANCE     8.553070 LB AT/MOLN2.    103.16 PERCENT
 HYDROGEN BALANCE    21.290554 LB AT/MOLN2.    102.72 PERCENT
 OXYGEN BALANCE       0.563752 LB AT/MOLN2.    106.03 PERCENT

 PERCENT O2 REACT     63.8857     PERCENT C4 REACT      8.9101

   CO       CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
            MOLE PRODUCT PER MOLE N-BUTANE
 0.3821  0.0939  0.3312  0.3812  0.4106  0.1851  0.6862  0.7566
            MOLE PRODUCT PER MOLE N-BUTENES
 1.1534  0.2836  1.0000  1.1508  1.2395  0.5588  2.0713  2.2840
            MOLE PRODUCT PER MOLE CO
 1.0000  0.2459  0.8669  0.9977  1.0746  0.4845  1.7957  1.9801
            MOLE PRODUCT PER MOLE ETHENE
 1.0641  0.2617  0.9225  1.0617  1.1435  0.5155  1.9109  2.1071
```

```
RUN NO =  66   SAMPLE NO =   3

PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
  1        0.711144       0.024922       0.098214       0.073403
  2        0.344286       0.012065       0.047548       0.035536
  3       28.534118       1.000000       3.940780       2.945241
  4        2.603590       0.091244       0.359575       0.268738
  5        2.186338       0.076621       0.301950       0.225670
  6        2.040808       0.071521       0.281851       0.210648
  7        0.606807       0.021266       0.083804       0.062633
  8        0.121839       0.004269       0.016826       0.012576
  9        2.030655       0.071165       0.280449       0.209600
 10        0.128525       0.004504       0.017750       0.013266
 11        0.751217       0.026327       0.103748       0.077539
 12        1.105054       0.038727       0.152616       0.114061
 13       49.452438       1.733098       6.829759       5.104393
 14        0.033360       0.001169       0.004607       0.003443
 15        0.017231       0.000603       0.002379       0.001778
 16        0.362979       0.012720       0.050130       0.037466
 17        5.816845       0.203855       0.803350       0.600404
 18        0.308799       0.010822       0.042647       0.031873
 19        1.561435       0.054721       0.215646       0.161168
 20        0.472348       0.016553       0.065234       0.048754
 21        0.072445       0.002538       0.010005       0.007477
 22        0.261596       0.009167       0.036128       0.027001
 23        0.036339       0.001273       0.005018       0.003750
 24        0.059320       0.002078       0.008192       0.006122
 25        0.074017       0.002593       0.010222       0.007639
 26        0.024020       0.000841       0.003317       0.002479
 27        0.026734       0.000936       0.003692       0.002759
 28        0.041441       0.001452       0.005723       0.004277
 29        0.192122       0.006733       0.026533       0.019830
 30        0.022303       0.000781       0.003080       0.002302

  TOTALS      99.999969      99.999984       3.504576

CARBON    BALANCE       7.995847 LB AT/MOLN2.      96.44 PERCENT
HYDROGEN BALANCE       20.056278 LB AT/MOLN2.      96.76 PERCENT
OXYGEN BALANCE          0.455170 LB AT/MOLN2.      85.61 PERCENT

PERCENT O2 REACT       95.4609     PERCENT C4 REACT      16.3816

   CO         CO2     BUTEN     PARFIN    ALCOHL    ALDHYD    OXYGCO    WATER
             MOLE  PRODUCT  PER MOLE  N-BUTANE
 0.2687    0.0374    0.1916    0.3742    0.1909    0.0895    0.3254    0.6004
             MOLE  PRODUCT  PER MOLE  N-BUTENES
 1.4025    0.1955    1.0000    1.9534    0.9966    0.4671    1.6985    3.1336
             MOLE  PRODUCT  PER MOLE  CO
 1.0000    0.1394    0.7129    1.3927    0.7105    0.3330    1.2109    2.2341
             MOLE  PRODUCT  PER MOLE  ETHENE
 1.2757    0.1778    0.9095    1.7768    0.9065    0.4249    1.5449    2.8502
```

```
RUN NO =  66  SAMPLE NO =  4

  PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
     1       0.681124      0.024399      0.096092      0.066706
     2       0.332485      0.011910      0.046906      0.032562
     3      27.915916      1.000000      3.938366      2.733984
     4       2.836228      0.101598      0.400133      0.277770
     5       2.365887      0.084750      0.333778      0.231706
     6       2.295572      0.082231      0.323858      0.224820
     7       0.817500      0.029284      0.115332      0.080063
     8       0.174100      0.006236      0.024562      0.017050
     9       1.938088      0.069425      0.273424      0.189809
    10       0.127111      0.004553      0.017932      0.012448
    11       0.730807      0.026178      0.103101      0.071572
    12       1.170438      0.041927      0.165125      0.114628
    13      47.648635      1.706862      6.722249      4.666536
    14       0.045719      0.001637      0.006450      0.004477
    15       0.027227      0.000975      0.003841      0.002666
    16       0.570790      0.020446      0.080526      0.055901
    17       7.147294      0.256029      1.008337      0.699980
    18       0.223866      0.008019      0.031582      0.021924
    19       1.468780      0.052614      0.207214      0.143847
    20       0.580070      0.020779      0.081836      0.056809
    21       0.099344      0.003558      0.014015      0.009729
    22       0.282037      0.010103      0.039789      0.027621
    23       0.031858      0.001141      0.004494      0.003120
    24       0.102518      0.003672      0.014463      0.010040
    25       0.099913      0.003579      0.014095      0.009785
    26       0.020092      0.000719      0.002834      0.001967
    27       0.025290      0.000905      0.003568      0.002476
    28       0.040517      0.001451      0.005716      0.003968
    29       0.180859      0.006478      0.025515      0.017712
    30       0.020083      0.000719      0.002833      0.001966

   TOTALS  100.000045     99.999984      3.582186

CARBON   BALANCE      7.984290 LB AT/MOLN2.    96.30 PERCENT
HYDROGEN BALANCE     20.082843 LB AT/MOLN2.    96.89 PERCENT
OXYGEN BALANCE        0.536084 LB AT/MOLN2.   100.83 PERCENT

PERCENT O2 REACT     95.5194     PERCENT C4 REACT     17.6474

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2777   0.0559   0.1862   0.3955   0.1732   0.0912   0.3109   0.6999
            MOLE  PRODUCT  PER MOLE  N-BUTENES
1.4917   0.3002   1.0000   2.1241   0.9304   0.4900   1.6700   3.7592
            MOLE  PRODUCT  PER MOLE  CO
1.0000   0.2012   0.6703   1.4239   0.6237   0.3285   1.1195   2.5199
            MOLE  PRODUCT  PER MOLE  ETHENE
1.2355   0.2486   0.8282   1.7593   0.7706   0.4058   1.3831   3.1135
```

```
RUN NO =  66   SAMPLE NO =  5

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1        0.822368      0.028506      0.112642      0.077042
    2        0.367814      0.012749      0.050380      0.034457
    3       28.848171      1.000000      3.951434      2.702589
    4        2.177479      0.075480      0.298256      0.203993
    5        2.111129      0.073180      0.289168      0.197777
    6        2.311686      0.080132      0.316639      0.216566
    7        0.789810      0.027378      0.108183      0.073991
    8        0.167591      0.005809      0.022955      0.015700
    9        0.784133      0.027181      0.107405      0.073460
   10        0.103311      0.003581      0.014150      0.009678
   11        1.243364      0.043100      0.170307      0.116482
   12        1.201871      0.041661      0.164624      0.112595
   13       49.117286      1.702613      6.727765      4.601464
   14        0.023837      0.000826      0.003265      0.002233
   15        0.017757      0.000615      0.002432      0.001663
   16        0.405336      0.014050      0.055520      0.037973
   17        6.897265      0.239088      0.944742      0.646157
   18        0.331956      0.011507      0.045469      0.031098
   19        1.252144      0.043404      0.171510      0.117304
   20        0.471424      0.016341      0.064572      0.044164
   21        0.254313      0.008815      0.034834      0.023824
   22        0.011474      0.000397      0.001571      0.001074
   23        0.011311      0.000392      0.001549      0.001059
   24        0.022990      0.000796      0.003149      0.002153
   25        0.049527      0.001716      0.006783      0.004639
   26        0.017092      0.000592      0.002341      0.001601
   27        0.033455      0.001159      0.004582      0.003134
   28        0.028052      0.000972      0.003842      0.002628
   29        0.114915      0.003983      0.015740      0.010765
   30        0.011305      0.000391      0.001548      0.001059

TOTALS      99.999954    100.000030      3.466425

CARBON   BALANCE     7.791213 LB AT/MOLN2.     93.97 PERCENT
HYDROGEN BALANCE    19.681510 LB AT/MOLN2.     94.95 PERCENT
OXYGEN BALANCE       0.458642 LB AT/MOLN2.     86.26 PERCENT

PERCENT O2 REACT      95.2035     PERCENT C4 REACT     17.8524

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2039   0.0379   0.2290   0.3645   0.1534   0.0805   0.2445   0.6461
           MOLE  PRODUCT  PER MOLE  N-BUTENES
0.8904   0.1657   1.0000   1.5912   0.6700   0.3516   1.0673   2.8206
           MOLE  PRODUCT  PER MOLE  CO
1.0000   0.1861   1.1229   1.7868   0.7524   0.3948   1.1986   3.1675
           MOLE  PRODUCT  PER MOLE  ETHENE
0.9419   0.1753   1.0577   1.6831   0.7087   0.3719   1.1290   2.9836
```

```
RUN NO =  67
REACTOR ENTRANCE CONDITIONS


AIR =   2.70 LB/HR              BUTANE =   6.55 LB/HR
TEMPERATURE =   684.00 DEG F
PRESSURE =  53.59 LB/SQ IN
OXYGEN = 9.5267 NITROGEN = 35.8386 BUTANE = 54.6346  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  1.5244  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   5.7348
DENSITY OF GAS MIXTURE =   0.1957 LB/CU FT
GAS VELOCITY =   6.15 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.56 SEC
REYNOLDS NUMBER =    4446
```

```
RUN NO =  67  SAMPLE NO =  1

  PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
     1        0.000000       0.000000       0.000000       0.000000
     2        7.673542       0.216631       4.403876       5.016197
     3       35.422088       1.000000      20.328876      23.155426
     4        0.199976       0.005645       0.114767       0.130724
     5        0.074151       0.002093       0.042555       0.048472
     6        0.051544       0.001455       0.029581       0.033694
     7        0.005744       0.000162       0.003297       0.003755
     8        0.005008       0.000141       0.002874       0.003273
     9        1.972891       0.055696       1.132250       1.289679
    10        0.130058       0.003671       0.074640       0.085019
    11        0.163370       0.004612       0.093758       0.106795
    12        0.069045       0.001949       0.039625       0.045134
    13       52.469818       1.481274      30.112632      34.299530
    14        0.021826       0.000616       0.012526       0.014268
    15        0.000000       0.000000       0.000000       0.000000
    16        0.813178       0.022956       0.466686       0.531574
    17        0.176423       0.004980       0.101249       0.115327
    18        0.151545       0.004278       0.086972       0.099065
    19        0.206876       0.005840       0.118727       0.135234
    20        0.052086       0.001470       0.029892       0.034049
    21        0.019272       0.000544       0.011060       0.012598
    22        0.273838       0.007730       0.157157       0.179008
    23        0.000000       0.000000       0.000000       0.000000
    24        0.047773       0.001348       0.027417       0.031229
    25        0.000000       0.000000       0.000000       0.000000
    26        0.000000       0.000000       0.000000       0.000000
    27        0.000000       0.000000       0.000000       0.000000
    28        0.000000       0.000000       0.000000       0.000000
    29        0.000000       0.000000       0.000000       0.000000
    30        0.000000       0.000000       0.000000       0.000000

  TOTALS    099.999999      99.999954       2.823096

CARBON   BALANCE     6.203589 LB AT/MOLN2.    101.73 PERCENT
HYDROGEN BALANCE    15.348619 LB AT/MOLN2.    100.68 PERCENT
OXYGEN BALANCE       0.511015 LB AT/MOLN2.     96.11 PERCENT

PERCENT O2 REACT      18.5052     PERCENT C4 REACT      2.8328

  CO        CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.1307   0.5315   0.1519   0.0555   0.1478   0.1643   0.4911   0.1153
           MOLE  PRODUCT  PER MOLE  N-BUTENES
0.8604   3.4988   1.0000   0.3653   0.9730   1.0817   3.2329   0.7590
           MOLE  PRODUCT  PER MOLE  CO
1.0000   4.0663   1.1622   0.4245   1.1308   1.2571   3.7574   0.8822
           MOLE  PRODUCT  PER MOLE  ETHENE
3.8797  15.7763   4.5090   1.6472   4.3874   4.8774  14.5776   3.4227
```

```
RUN NO =   67   SAMPLE NO =   2

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
   1        1.870375       0.056812       0.311195       0.300598
   2        2.741068       0.083259       0.456061       0.440532
   3       32.921821       1.000000       5.477568       5.291049
   4        4.767739       0.144820       0.793261       0.766249
   5        1.531762       0.046527       0.254856       0.246178
   6        2.276088       0.069136       0.378698       0.365802
   7        0.305517       0.009280       0.050832       0.049101
   8        0.018727       0.000568       0.003115       0.003009
   9        0.927462       0.028171       0.154312       0.149057
  10        0.095899       0.002912       0.015955       0.015412
  11        0.249209       0.007569       0.041463       0.040051
  12        1.273913       0.038695       0.211955       0.204737
  13       43.965835       1.335462       7.315083       7.065993
  14        0.010723       0.000325       0.001784       0.001723
  15        0.014491       0.000440       0.002411       0.002329
  16        0.618791       0.018795       0.102955       0.099449
  17        3.799139       0.115398       0.632104       0.610580
  18        0.228242       0.006932       0.037975       0.036682
  19        1.300024       0.039488       0.216299       0.208934
  20        0.441048       0.013396       0.073382       0.070883
  21        0.032586       0.000989       0.005421       0.005237
  22        0.195483       0.005937       0.032524       0.031417
  23        0.047630       0.001446       0.007924       0.007654
  24        0.067940       0.002063       0.011303       0.010919
  25        0.068625       0.002084       0.011417       0.011029
  26        0.015466       0.000469       0.002573       0.002485
  27        0.016693       0.000507       0.002777       0.002682
  28        0.018689       0.000567       0.003109       0.003003
  29        0.179114       0.005440       0.029801       0.028786
  30        0.000000       0.000000       0.000000       0.000000

  TOTALS   99.999969      99.999969       3.037497

CARBON    BALANCE     6.127145 LB AT/MOLN2.    100.48 PERCENT
HYDROGEN BALANCE     15.155858 LB AT/MOLN2.     99.41 PERCENT
OXYGEN BALANCE        0.543655 LB AT/MOLN2.    102.25 PERCENT

PERCENT O2 REACT     68.6784     PERCENT C4 REACT     12.3977

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE PRODUCT PER MOLE N-BUTANE
0.7662   0.0994   0.2447   0.5988   0.2454   0.1211   0.4197   0.6105
           MOLE PRODUCT PER MOLE N-BUTENES
3.1302   0.4062   1.0000   2.4465   1.0026   0.4949   1.7145   2.4943
           MOLE PRODUCT PER MOLE CO
1.0000   0.1297   0.3194   0.7815   0.3203   0.1581   0.5477   0.7968
           MOLE PRODUCT PER MOLE ETHENE
2.0947   0.2718   0.6691   1.6371   0.6709   0.3312   1.1473   1.6691
```

```
RUN NO =  67  SAMPLE NO =  3

 PRD NO  MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
   1        1.006406      0.030371      0.120081      0.118483
   2        0.427317      0.012895      0.050986      0.050307
   3       33.136169      1.000000      3.953711      3.901108
   4        3.304882      0.099736      0.394328      0.389082
   5        2.839341      0.085687      0.338782      0.334274
   6        1.981892      0.059810      0.236473      0.233327
   7        0.710594      0.021444      0.084786      0.083657
   8        0.027698      0.000835      0.003304      0.003260
   9        0.882223      0.026624      0.105264      0.103863
  10        0.101210      0.003054      0.012076      0.011915
  11        0.384807      0.011612      0.045914      0.045303
  12        1.195314      0.036072      0.142621      0.140723
  13       42.020736      1.268123      5.013792      4.947085
  14        0.028209      0.000851      0.003365      0.003321
  15        0.019359      0.000584      0.002309      0.002279
  16        0.393232      0.011867      0.046919      0.046295
  17        8.421228      0.254140      1.004796      0.991427
  18        0.312216      0.009422      0.037252      0.036757
  19        1.468082      0.044304      0.175167      0.172836
  20        0.471353      0.014224      0.056240      0.055492
  21        0.056059      0.001691      0.006688      0.006599
  22        0.225477      0.006804      0.026903      0.026545
  23        0.056456      0.001703      0.006736      0.006646
  24        0.072959      0.002201      0.008705      0.008589
  25        0.111073      0.003352      0.013252      0.013076
  26        0.020355      0.000614      0.002428      0.002396
  27        0.012979      0.000391      0.001548      0.001528
  28        0.064640      0.001950      0.007712      0.007610
  29        0.219899      0.006636      0.026237      0.025888
  30        0.028030      0.000845      0.003344      0.003300

  TOTALS   99.999969    100.000030      3.017852

CARBON   BALANCE    5.889678 LB AT/MOLN2.    96.58 PERCENT
HYDROGEN BALANCE   14.995624 LB AT/MOLN2.    98.36 PERCENT
OXYGEN BALANCE      0.497546 LB AT/MOLN2.    93.58 PERCENT

PERCENT O2 REACT    95.1487    PERCENT C4 REACT    16.8149

  CO       CO2    BUTEN   PARFIN  ALCOHL  ALDHYD  OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.3890  0.0462  0.1860  0.5396  0.2077  0.1023  0.3672  0.9914
          MOLE PRODUCT PER MOLE N-BUTENES
2.0915  0.2488  1.0000  2.9010  1.1166  0.5502  1.9742  5.3294
          MOLE PRODUCT PER MOLE CO
1.0000  0.1189  0.4781  1.3870  0.5338  0.2630  0.9439  2.5481
          MOLE PRODUCT PER MOLE ETHENE
1.6675  0.1984  0.7972  2.3129  0.8902  0.4387  1.5740  4.2490
```

```
RUN NO =  67  SAMPLE NO =  4

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1        1.653044      0.049694      0.197557      0.329111
    2        0.475015      0.014280      0.056769      0.094572
    3       33.264389      1.000000      3.975468      6.622746
    4        3.450763      0.103737      0.412405      0.687026
    5        2.698674      0.081128      0.322521      0.537290
    6        1.625840      0.048876      0.194306      0.323695
    7        0.668292      0.020090      0.079868      0.133053
    8        0.035120      0.001055      0.004197      0.006992
    9        1.011212      0.030399      0.120851      0.201326
   10        0.114075      0.003429      0.013633      0.022711
   11        0.579741      0.017428      0.069285      0.115423
   12        1.086466      0.032661      0.129844      0.216309
   13       45.687492      1.373465      5.460168      9.096113
   14        0.032763      0.000984      0.003915      0.006522
   15        0.013449      0.000404      0.001607      0.002677
   16        0.364984      0.010972      0.043619      0.072666
   17        4.586176      0.137870      0.548099      0.913081
   18        0.283749      0.008530      0.033911      0.056492
   19        1.330731      0.040004      0.159037      0.264940
   20        0.332381      0.009992      0.039723      0.066175
   21        0.035392      0.001063      0.004229      0.007046
   22        0.274655      0.008256      0.032824      0.054682
   23        0.020519      0.000616      0.002452      0.004085
   24        0.071603      0.002152      0.008557      0.014255
   25        0.058530      0.001759      0.006995      0.011653
   26        0.021979      0.000660      0.002626      0.004376
   27        0.013590      0.000408      0.001624      0.002705
   28        0.030095      0.000904      0.003596      0.005991
   29        0.160211      0.004816      0.019147      0.031897
   30        0.019304      0.000580      0.002307      0.003843

 TOTALS     099.999999    100.000061      3.006219

CARBON   BALANCE      6.273664 LB AT/MOLN2.    102.88 PERCENT
HYDROGEN BALANCE     15.748727 LB AT/MOLN2.    103.30 PERCENT
OXYGEN  BALANCE       0.371859 LB AT/MOLN2.     69.94 PERCENT

PERCENT O2 REACT      94.6280     PERCENT C4 REACT       9.9048

  CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.6870  0.0726   0.3317   1.0064   0.3082   0.1396   0.5281   0.9130
          MOLE  PRODUCT  PER MOLE  N-BUTENES
2.0710  0.2190   1.0000   3.0339   0.9292   0.4209   1.5920   2.7524
          MOLE  PRODUCT  PER MOLE  CO
1.0000  0.1057   0.4828   1.4649   0.4486   0.2032   0.7687   1.3290
          MOLE  PRODUCT  PER MOLE  ETHENE
2.1224  0.2244   1.0248   3.1092   0.9523   0.4313   1.6316   2.8208
```

```
      RUN NO =   67   SAMPLE NO =   5

       PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
          1        1.167412      0.035956      0.142180      0.143773
          2        0.419878      0.012932      0.051137      0.051710
          3       32.467681      1.000000      3.954281      3.998578
          4        3.685602      0.113516      0.448874      0.453902
          5        3.147505      0.096942      0.383338      0.387633
          6        2.257431      0.069528      0.274935      0.278015
          7        0.655603      0.020192      0.079846      0.080741
          8        0.040008      0.001232      0.004872      0.004927
          9        1.385786      0.042682      0.168776      0.170667
         10        0.111754      0.003442      0.013610      0.013763
         11        0.554604      0.017081      0.067545      0.068302
         12        1.400357      0.043130      0.170551      0.172461
         13       41.375885      1.274371      5.039222      5.095673
         14        0.029720      0.000915      0.003619      0.003660
         15        0.024354      0.000750      0.002966      0.002999
         16        0.487605      0.015018      0.059386      0.060051
         17        7.633905      0.235123      0.929743      0.940158
         18        0.230591      0.007102      0.028084      0.028398
         19        1.639491      0.050496      0.199675      0.201912
         20        0.447784      0.013791      0.054536      0.055147
         21        0.037294      0.001148      0.004542      0.004593
         22        0.236745      0.007291      0.028833      0.029156
         23        0.017279      0.000532      0.002104      0.002128
         24        0.130028      0.004004      0.015836      0.016013
         25        0.074301      0.002288      0.009049      0.009150
         26        0.026042      0.000802      0.003171      0.003207
         27        0.029688      0.000914      0.003615      0.003656
         28        0.031590      0.000972      0.003847      0.003890
         29        0.232120      0.007149      0.028270      0.028586
         30        0.022106      0.000680      0.002692      0.002722

      TOTALS     100.000045    100.000015      3.079986

 CARBON    BALANCE      6.062321 LB AT/MOLN2.     99.41 PERCENT
 HYDROGEN BALANCE      15.326272 LB AT/MOLN2.    100.53 PERCENT
 OXYGEN BALANCE         0.501715 LB AT/MOLN2.     94.37 PERCENT

 PERCENT O2 REACT      95.1350     PERCENT C4 REACT     16.4050

   CO       CO2     BUTEN     PARFIN   ALCOHL    ALDHYD    OXYGCO    WATER
           MOLE   PRODUCT  PER MOLE  N-BUTANE
 0.4539   0.0600   0.2407    0.6170   0.2382    0.1032    0.3885    0.9401
           MOLE   PRODUCT  PER MOLE  N-BUTENES
 1.8852   0.2494   1.0000    2.5629   0.9897    0.4287    1.6138    3.9048
           MOLE   PRODUCT  PER MOLE  CO
 1.0000   0.1322   0.5304    1.3594   0.5250    0.2273    0.8560    2.0712
           MOLE   PRODUCT  PER MOLE  ETHENE
 1.6326   0.2160   0.8660    2.2195   0.8571    0.3712    1.3976    3.3816
```

```
RUN NO =  68
REACTOR ENTRANCE CONDITIONS


AIR =    2.42 LB/HR              BUTANE =    8.20 LB/HR
TEMPERATURE =   692.00 DEG F
PRESSURE =  53.71 LB/SQ IN
OXYGEN = 7.8295 NITROGEN = 29.4540 BUTANE = 62.7164  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.1293  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   8.0102
DENSITY OF GAS MIXTURE =   0.2051 LB/CU FT
GAS VELOCITY =   6.74 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.43 SEC
REYNOLDS NUMBER =    5357
```

```
RUN NO =  68   SAMPLE NO =  1

 PRD NO   MOL PERCENT    MOLS/MOL N2   MOLS/MOXY R    MOLS/MBUT R
    1       0.000000       0.000000      0.000000       0.000000
    2       7.060018       0.241592      9.970903      21.400512
    3      29.222785       1.000000     41.271507      88.580871
    4       0.049888       0.001707      0.070458       0.151224
    5       0.065846       0.002253      0.092995       0.199595
    6       0.025196       0.000862      0.035585       0.076375
    7       0.009248       0.000316      0.013061       0.028034
    8       0.011163       0.000382      0.015766       0.033840
    9       0.641188       0.021941      0.905553       1.943585
   10       0.183626       0.006283      0.259336       0.556612
   11       0.020181       0.000690      0.028502       0.061175
   12       0.010828       0.000370      0.015293       0.032823
   13      61.894195       2.118011     87.413513     187.615295
   14       0.000000       0.000000      0.000000       0.000000
   15       0.000000       0.000000      0.000000       0.000000
   16       0.055432       0.001896      0.078286       0.168027
   17       0.021847       0.000747      0.030855       0.066225
   18       0.184541       0.006314      0.260629       0.559387
   19       0.079098       0.002706      0.111711       0.239765
   20       0.035055       0.001199      0.049509       0.106262
   21       0.000000       0.000000      0.000000       0.000000
   22       0.369497       0.012644      0.521843       1.120030
   23       0.000000       0.000000      0.000000       0.000000
   24       0.060471       0.002069      0.085403       0.183302
   25       0.000000       0.000000      0.000000       0.000000
   26       0.000000       0.000000      0.000000       0.000000
   27       0.000000       0.000000      0.000000       0.000000
   28       0.000000       0.000000      0.000000       0.000000
   29       0.000000       0.000000      0.000000       0.000000
   30       0.000000       0.000000      0.000000       0.000000

 TOTALS   100.000015     100.000030      3.421988

CARBON   BALANCE     8.619522 LB AT/MOLN2.   101.20 PERCENT
HYDROGEN BALANCE    21.493236 LB AT/MOLN2.   100.94 PERCENT
OXYGEN BALANCE       0.514369 LB AT/MOLN2.    96.75 PERCENT

PERCENT O2 REACT      9.1150     PERCENT C4 REACT      0.5301

  CO       CO2    BUTEN    PARFIN   ALCOHL  ALDHYD   OXYGCO    WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.1512  0.1680   0.0939   0.2614   0.2397  0.8489   2.2087   0.0662
          MOLE  PRODUCT  PER MOLE  N-BUTENES
1.6087  1.7875   1.0000   2.7816   2.5507  9.0314  23.4974   0.7045
          MOLE  PRODUCT  PER MOLE  CO
1.0000  1.1111   0.6215   1.7290   1.5854  5.6138  14.6057   0.4379
          MOLE  PRODUCT  PER MOLE  ETHENE
1.9799  2.1999   1.2307   3.4234   3.1392 11.1154  28.9194   0.8670
```

```
RUN NO =   68   SAMPLE NO =   2

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
  1        0.130325      0.004434      0.036614      0.027010
  2        4.253040      0.144711      1.194865      0.881458
  3       29.389774      1.000000      8.256877      6.091139
  4        1.218770      0.041469      0.342405      0.252594
  5        0.702383      0.023898      0.197330      0.145571
  6        0.544775      0.018536      0.153051      0.112906
  7        0.050789      0.001728      0.014268      0.010526
  8        0.011385      0.000387      0.003198      0.002359
  9        0.978931      0.033308      0.275024      0.202887
 10        0.126504      0.004304      0.035540      0.026218
 11        0.171018      0.005818      0.048046      0.035444
 12        0.861983      0.029329      0.242168      0.178649
 13       57.754661      1.965127     16.225822     11.969867
 14        0.012158      0.000413      0.003415      0.002519
 15        0.003054      0.000103      0.000858      0.000633
 16        0.290889      0.009897      0.081723      0.060287
 17        1.024562      0.034861      0.287844      0.212344
 18        0.142697      0.004855      0.040090      0.029574
 19        1.368448      0.046562      0.384457      0.283615
 20        0.332496      0.011313      0.093412      0.068911
 21        0.038416      0.001307      0.010792      0.007961
 22        0.259388      0.008825      0.072873      0.053759
 23        0.004015      0.000136      0.001128      0.000832
 24        0.052421      0.001783      0.014727      0.010864
 25        0.048567      0.001652      0.013644      0.010065
 26        0.007092      0.000241      0.001992      0.001469
 27        0.007518      0.000255      0.002112      0.001558
 28        0.014159      0.000481      0.003978      0.002934
 29        0.187503      0.006379      0.052677      0.038860
 30        0.012385      0.000421      0.003479      0.002566

   TOTALS     99.999923     99.999923      3.402543

CARBON   BALANCE     8.374593 LB AT/MOLN2.     98.32 PERCENT
HYDROGEN BALANCE    20.826858 LB AT/MOLN2.     97.81 PERCENT
OXYGEN BALANCE       0.469765 LB AT/MOLN2.     88.36 PERCENT

PERCENT O2 REACT       45.5608    PERCENT C4 REACT      7.7101

   CO        CO2     BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
            MOLE PRODUCT PER MOLE N-BUTANE
 0.2525    0.0602   0.2140   0.1854   0.3319   0.1109   0.5129   0.2123
            MOLE PRODUCT PER MOLE N-BUTENES
 1.1798    0.2815   1.0000   0.8662   1.5502   0.5180   2.3960   0.9918
            MOLE PRODUCT PER MOLE CO
 1.0000    0.2386   0.8475   0.7342   1.3139   0.4390   2.0308   0.8406
            MOLE PRODUCT PER MOLE ETHENE
 2.2371    0.5339   1.8961   1.6426   2.9396   0.9823   4.5433   1.8807
```

```
RUN NO =  68   SAMPLE NO =  3

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
  1        0.734781      0.025177      0.100592      0.068240
  2        0.453102      0.015525      0.062030      0.042080
  3       29.183528      1.000000      3.995258      2.710327
  4        2.627480      0.090032      0.359705      0.244018
  5        1.924935      0.065959      0.263525      0.178772
  6        1.693382      0.058025      0.231826      0.157267
  7        0.358307      0.012277      0.049052      0.033276
  8        0.018255      0.000625      0.002499      0.001695
  9        1.004846      0.034431      0.137564      0.093321
 10        0.131684      0.004512      0.018027      0.012229
 11        0.438242      0.015016      0.059995      0.040700
 12        0.979638      0.033568      0.134113      0.090980
 13       51.372978      1.760341      7.033019      4.771100
 14        0.032603      0.001117      0.004463      0.003027
 15        0.027348      0.000937      0.003744      0.002539
 16        0.369206      0.012651      0.050544      0.034288
 17        5.155985      0.176674      0.705860      0.478845
 18        0.191391      0.006558      0.026201      0.017774
 19        1.918674      0.065745      0.262668      0.178190
 20        0.517634      0.017737      0.070864      0.048073
 21        0.059864      0.002051      0.008195      0.005559
 22        0.246394      0.008442      0.033731      0.022883
 23        0.045532      0.001560      0.006233      0.004228
 24        0.105162      0.003603      0.014396      0.009766
 25        0.058143      0.001992      0.007959      0.005399
 26        0.028982      0.000993      0.003967      0.002691
 27        0.017357      0.000594      0.002376      0.001612
 28        0.038230      0.001310      0.005233      0.003550
 29        0.230481      0.007897      0.031553      0.021405
 30        0.036039      0.001234      0.004933      0.003347

  TOTALS      99.999969    100.000045      3.426592

CARBON   BALANCE      7.878467 LB AT/MOLN2.      92.50 PERCENT
HYDROGEN BALANCE     19.802715 LB AT/MOLN2.      93.00 PERCENT
OXYGEN BALANCE        0.442782 LB AT/MOLN2.      83.28 PERCENT

PERCENT O2 REACT      94.1592     PERCENT C4 REACT      17.3277

  CO       CO2     BUTEN    PARFIN    ALCOHL    ALDHYD    OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2440   0.0342   0.1316    0.2819    0.2078    0.0772    0.3244    0.4788
           MOLE  PRODUCT  PER MOLE  N-BUTENES
1.8531   0.2603   1.0000    2.1414    1.5784    0.5864    2.4641    3.6364
           MOLE  PRODUCT  PER MOLE  CO
1.0000   0.1405   0.5396    1.1555    0.8517    0.3164    1.3297    1.9623
           MOLE  PRODUCT  PER MOLE  ETHENE
1.5516   0.2180   0.8373    1.7930    1.3216    0.4910    2.0632    3.0447
```

```
RUN NO =   68   SAMPLE NO =   4

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
  1        0.427013      0.014772      0.058848      0.040805
  2        0.427775      0.014798      0.058953      0.040878
  3       28.906398      1.000000      3.983683      2.762290
  4        2.873094      0.099393      0.395950      0.274552
  5        2.319273      0.080233      0.319626      0.221629
  6        1.634071      0.056529      0.225196      0.156151
  7        0.555669      0.019223      0.076578      0.053099
  8        0.030003      0.001037      0.004134      0.002867
  9        1.410427      0.048792      0.194375      0.134780
 10        0.119659      0.004139      0.016490      0.011434
 11        0.444931      0.015392      0.061317      0.042517
 12        1.047393      0.036233      0.144344      0.100088
 13       51.085769      1.767282      7.040291      4.881748
 14        0.037147      0.001285      0.005119      0.003549
 15        0.017412      0.000602      0.002399      0.001663
 16        0.355509      0.012298      0.048993      0.033972
 17        4.924702      0.170367      0.678688      0.470603
 18        0.302620      0.010468      0.041705      0.028918
 19        1.805202      0.062449      0.248780      0.172504
 20        0.378032      0.013077      0.052097      0.036124
 21        0.084788      0.002933      0.011685      0.008102
 22        0.304273      0.010526      0.041932      0.029076
 23        0.023066      0.000797      0.003178      0.002204
 24        0.106652      0.003689      0.014698      0.010191
 25        0.076180      0.002635      0.010498      0.007279
 26        0.019358      0.000669      0.002667      0.001849
 27        0.021668      0.000749      0.002986      0.002070
 28        0.030518      0.001055      0.004205      0.002916
 29        0.203338      0.007034      0.028022      0.019430
 30        0.028205      0.000975      0.003887      0.002695

 TOTALS   99.999954     99.999969      3.459443

CARBON   BALANCE     7.984902 LB AT/MOLN2.     93.75 PERCENT
HYDROGEN BALANCE    20.012500 LB AT/MOLN2.     93.98 PERCENT
OXYGEN BALANCE       0.441018 LB AT/MOLN2.     82.95 PERCENT

PERCENT O2 REACT     94.4328    PERCENT C4 REACT     17.0017

  CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
           MOLE PRODUCT PER MOLE N-BUTANE
0.2745   0.0339   0.1426   0.3184   0.2018   0.0773   0.3233   0.4706
           MOLE PRODUCT PER MOLE N-BUTENES
1.9252   0.2382   1.0000   2.2327   1.4157   0.5420   2.2675   3.3000
           MOLE PRODUCT PER MOLE CO
1.0000   0.1237   0.5194   1.1597   0.7353   0.2815   1.1777   1.7140
           MOLE PRODUCT PER MOLE ETHENE
1.7582   0.2175   0.9132   2.0390   1.2928   0.4950   2.0708   3.0137
```

```
RUN NO =   68   SAMPLE NO =    5

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
   1        1.041387      0.035832      0.144240      0.090815
   2        0.505673      0.017399      0.070039      0.044097
   3       29.062511      1.000000      4.025389      2.534433
   4        2.767229      0.095216      0.383283      0.241319
   5        2.380744      0.081918      0.329752      0.207615
   6        1.761209      0.060600      0.243941      0.153588
   7        0.625104      0.021508      0.086581      0.054513
   8        0.020977      0.000721      0.002905      0.001829
   9        0.831714      0.028618      0.115199      0.072530
  10        0.141815      0.004879      0.019642      0.012367
  11        0.211916      0.007291      0.029352      0.018480
  12        1.390697      0.047851      0.192622      0.121277
  13       50.415763      1.734735      6.982983      4.396570
  14        0.034876      0.001200      0.004830      0.003041
  15        0.018551      0.000638      0.002569      0.001617
  16        0.369285      0.012706      0.051149      0.032204
  17        5.202730      0.179018      0.720619      0.453710
  18        0.136239      0.004687      0.018870      0.011880
  19        1.836131      0.063178      0.254318      0.160122
  20        0.428157      0.014732      0.059303      0.037338
  21        0.040612      0.001397      0.005625      0.003541
  22        0.305550      0.010513      0.042321      0.026645
  23        0.034125      0.001174      0.004726      0.002975
  24        0.085382      0.002937      0.011826      0.007445
  25        0.073451      0.002527      0.010173      0.006405
  26        0.023596      0.000811      0.003268      0.002057
  27        0.033638      0.001157      0.004659      0.002933
  28        0.019569      0.000673      0.002710      0.001706
  29        0.173429      0.005967      0.024021      0.015124
  30        0.028064      0.000965      0.003887      0.002447

 TOTALS    99.999969     99.999954      3.440858

CARBON   BALANCE     7.810264 LB AT/MOLN2.     91.69 PERCENT
HYDROGEN BALANCE    19.669914 LB AT/MOLN2.     92.37 PERCENT
OXYGEN BALANCE       0.445172 LB AT/MOLN2.     83.73 PERCENT

PERCENT O2 REACT      93.4544    PERCENT C4 REACT    18.5302

  CO       CO2     BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
           MOLE PRODUCT PER MOLE N-BUTANE
0.2413   0.0322   0.1397   0.3547   0.1808   0.0595   0.2806   0.4537
           MOLE PRODUCT PER MOLE N-BUTENES
1.7266   0.2304   1.0000   2.5384   1.2939   0.4264   2.0079   3.2464
           MOLE PRODUCT PER MOLE CO
1.0000   0.1334   0.5791   1.4701   0.7494   0.2469   1.1628   1.8801
           MOLE PRODUCT PER MOLE ETHENE
1.5712   0.2096   0.9099   2.3098   1.1774   0.3880   1.8271   2.9540
```

```
RUN NO =   71
REACTOR ENTRANCE CONDITIONS
                                BUTANE =  10.00 LB/HR
 AIR =   2.20 LB/HR
 TEMPERATURE =   698.00 DEG F
 PRESSURE =  51.40 LB/SQ IN
 OXYGEN = 6.4485 NITROGEN = 24.2588 BUTANE = 69.2925  MOL PCNT
 OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.8563  MOLS/MN2
 BUTANE TO OXYGEN MOLAR RATIO =  10.7454
 DENSITY OF GAS MIXTURE =  0.2032 LB/CU FT
 GAS VELOCITY =   7.82 FT/SEC
 RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.23 SEC
 REYNOLDS NUMBER =    6402
```

```
RUN NO =   71   SAMPLE NO =   1

 PRD NO   MOL  PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
   1         0.000000       0.000000       0.000000       0.000000
   2         4.466441       0.188671       2.445493       2.862056
   3        23.673061       1.000000      12.961620      15.169492
   4         0.504902       0.021328       0.276447       0.323536
   5         0.171084       0.007226       0.093673       0.109629
   6         0.222409       0.009395       0.121775       0.142518
   7         0.047903       0.002023       0.026228       0.030696
   8         0.023688       0.001000       0.012970       0.015179
   9         0.834239       0.035240       0.456768       0.534573
  10         0.220949       0.009333       0.120975       0.141582
  11         0.196484       0.008299       0.107580       0.125905
  12         0.632614       0.026722       0.346372       0.405373
  13        66.058685       2.790458      36.168853      42.329833
  14         0.000000       0.000000       0.000000       0.000000
  15         0.000000       0.000000       0.000000       0.000000
  16         0.179638       0.007588       0.098356       0.115110
  17         0.807959       0.034129       0.442378       0.517733
  18         0.171851       0.007259       0.094093       0.110120
  19         0.902382       0.038118       0.494078       0.578239
  20         0.142074       0.006001       0.077789       0.091040
  21         0.071340       0.003013       0.039060       0.045714
  22         0.416640       0.017599       0.228121       0.266979
  23         0.000000       0.000000       0.000000       0.000000
  24         0.060948       0.002574       0.033371       0.039055
  25         0.028357       0.001197       0.015526       0.018171
  26         0.000000       0.000000       0.000000       0.000000
  27         0.000000       0.000000       0.000000       0.000000
  28         0.000000       0.000000       0.000000       0.000000
  29         0.166434       0.007030       0.091127       0.106649
  30         0.000000       0.000000       0.000000       0.000000

     TOTALS     99.999938      99.999969       4.224208

 CARBON    BALANCE    11.644998 LB AT/MOLN2.    101.92 PERCENT
 HYDROGEN BALANCE     29.016830 LB AT/MOLN2.    101.58 PERCENT
 OXYGEN BALANCE        0.530773 LB AT/MOLN2.     99.83 PERCENT

 PERCENT O2 REACT        29.0234    PERCENT C4 REACT         2.3078

    CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
              MOLE PRODUCT PER MOLE N-BUTANE
  0.3235   0.1151   0.5312   0.1555   0.7306   0.2402   1.2559   0.5177
              MOLE PRODUCT PER MOLE N-BUTENES
  0.6089   0.2166   1.0000   0.2926   1.3751   0.4521   2.3640   0.9745
              MOLE PRODUCT PER MOLE CO
  1.0000   0.3557   1.6420   0.4806   2.2581   0.7424   3.8819   1.6002
              MOLE PRODUCT PER MOLE ETHENE
  2.2701   0.8076   3.7278   1.0911   5.1263   1.6855   8.8126   3.6327
```

```
RUN NO =  71   SAMPLE NO =  2

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
  1        0.000000      0.000000      0.000000      0.000000
  2        2.812016      0.120228      0.825783      0.586532
  3       23.388839      1.000000      6.868428      4.878459
  4        0.936346      0.040033      0.274970      0.195303
  5        0.940811      0.040224      0.276281      0.196235
  6        0.857326      0.036655      0.251764      0.178821
  7        0.278786      0.011919      0.081869      0.058149
  8        0.053351      0.002281      0.015667      0.011128
  9        1.321080      0.056483      0.387951      0.275551
 10        0.207224      0.008859      0.060854      0.043222
 11        0.195730      0.008368      0.057478      0.040825
 12        0.981209      0.041952      0.288144      0.204661
 13       62.013092      2.651397     18.210929     12.934732
 14        0.057907      0.002475      0.017005      0.012078
 15        0.035779      0.001529      0.010507      0.007462
 16        0.310660      0.013282      0.091229      0.064797
 17        2.468503      0.105541      0.724907      0.514882
 18        0.253112      0.010821      0.074329      0.052794
 19        1.795644      0.076773      0.527313      0.374536
 20        0.226163      0.009669      0.066415      0.047173
 21        0.089262      0.003816      0.026212      0.018618
 22        0.346783      0.014826      0.101837      0.072332
 23        0.020699      0.000885      0.006078      0.004317
 24        0.075858      0.003243      0.022276      0.015822
 25        0.028898      0.001235      0.008486      0.006027
 26        0.060266      0.002576      0.017697      0.012570
 27        0.044387      0.001897      0.013034      0.009258
 28        0.000000      0.000000      0.000000      0.000000
 29        0.200421      0.008569      0.058856      0.041804
 30        0.000000      0.000000      0.000000      0.000000

 TOTALS   99.999969     99.999984      4.275542

CARBON   BALANCE      11.436744 LB AT/MOLN2.    100.09 PERCENT
HYDROGEN BALANCE      28.598785 LB AT/MOLN2.    100.12 PERCENT
OXYGEN BALANCE         0.546913 LB AT/MOLN2.    102.87 PERCENT

PERCENT O2 REACT      54.7710     PERCENT C4 REACT        7.1763

   CO        CO2     BUTEN    PARFIN    ALCOHL    ALDHYD    OXYGCO    WATER
           MOLE PRODUCT PER MOLE N-BUTANE
 0.1953    0.0647    0.2454    0.2655    0.4475    0.1250    0.6552    0.5148
           MOLE PRODUCT PER MOLE N-BUTENES
 0.7955    0.2639    1.0000    1.0815    1.8230    0.5093    2.6692    2.0973
           MOLE PRODUCT PER MOLE CO
 1.0000    0.3317    1.2569    1.3594    2.2914    0.6402    3.3550    2.6363
           MOLE PRODUCT PER MOLE ETHENE
 1.0921    0.3623    1.3728    1.4847    2.5026    0.6992    3.6642    2.8793
```

```
RUN NO =  71  SAMPLE NO =  3

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
  1        0.000000      0.000000      0.000000      0.000000
  2        1.377619      0.057874      0.278309      0.207748
  3       23.803764      1.000000      4.808878      3.589667
  4        1.368247      0.057480      0.276415      0.206335
  5        0.970703      0.040779      0.196103      0.146384
  6        0.880527      0.036991      0.177885      0.132785
  7        0.327966      0.013777      0.066256      0.049458
  8        0.096843      0.004068      0.019564      0.014604
  9        0.528137      0.022187      0.106695      0.079644
 10        0.166692      0.007002      0.033675      0.025137
 11        0.242745      0.010197      0.049039      0.036606
 12        1.484827      0.062377      0.299967      0.223915
 13       61.361396      2.577802     12.396339      9.253454
 14        0.046247      0.001942      0.009343      0.006974
 15        0.046247      0.001942      0.009343      0.006974
 16        0.239803      0.010074      0.048445      0.036162
 17        3.051688      0.128201      0.616507      0.460202
 18        0.263576      0.011072      0.053248      0.039748
 19        2.269981      0.095362      0.458585      0.342318
 20        0.344065      0.014454      0.069508      0.051885
 21        0.039928      0.001677      0.008066      0.006021
 22        0.448308      0.018833      0.090568      0.067606
 23        0.050191      0.002108      0.010139      0.007568
 24        0.151750      0.006375      0.030656      0.022884
 25        0.051257      0.002153      0.010355      0.007729
 26        0.071113      0.002987      0.014366      0.010724
 27        0.050699      0.002129      0.010242      0.007645
 28        0.044181      0.001856      0.008925      0.006662
 29        0.221654      0.009311      0.044779      0.033426
 30        0.000000      0.000000      0.000000      0.000000

TOTALS    99.999969    100.000015      4.201014

CARBON   BALANCE     11.207918 LB AT/MOLN2.     98.09 PERCENT
HYDROGEN BALANCE     28.052299 LB AT/MOLN2.     98.20 PERCENT
OXYGEN BALANCE        0.489900 LB AT/MOLN2.     92.14 PERCENT

PERCENT O2 REACT     78.2283     PERCENT C4 REACT      9.7528

   CO       CO2     BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE PRODUCT PER MOLE N-BUTANE
 0.2063   0.0361   0.2605   0.2104   0.3924   0.1221   0.6042   0.4602
            MOLE PRODUCT PER MOLE N-BUTENES
 0.7920   0.1388   1.0000   0.8077   1.5065   0.4689   2.3192   1.7664
            MOLE PRODUCT PER MOLE CO
 1.0000   0.1752   1.2626   1.0199   1.9021   0.5920   2.9283   2.2303
            MOLE PRODUCT PER MOLE ETHENE
 1.5538   0.2723   1.9619   1.5848   2.9558   0.9200   4.5503   3.4657
```

```
RUN NO =   71   SAMPLE NO =   4

PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
   1       0.000000      0.000000      0.000000      0.000000
   2       0.558882      0.023423      0.096629      0.079782
   3      23.860351      1.000000      4.125419      3.406154
   4       1.872119      0.078461      0.323686      0.267252
   5       1.078356      0.045194      0.186446      0.153939
   6       1.004668      0.042106      0.173705      0.143420
   7       0.343382      0.014391      0.059370      0.049019
   8       0.119448      0.005006      0.020652      0.017051
   9       0.681931      0.028580      0.117904      0.097348
  10       0.159912      0.006702      0.027648      0.022828
  11       0.169361      0.007098      0.029282      0.024176
  12       1.143559      0.047927      0.197719      0.163247
  13      61.149147      2.562793     10.572595      8.729269
  14       0.022594      0.000946      0.003906      0.003225
  15       0.035493      0.001487      0.006136      0.005066
  16       0.339682      0.014236      0.058730      0.048490
  17       3.467437      0.145322      0.599514      0.494989
  18       0.170752      0.007156      0.029522      0.024375
  19       2.153286      0.090245      0.372299      0.307389
  20       0.321944      0.013492      0.055663      0.045958
  21       0.134343      0.005630      0.023227      0.019178
  22       0.564551      0.023660      0.097610      0.080591
  23       0.080249      0.003363      0.013875      0.011455
  24       0.122932      0.005152      0.021254      0.017549
  25       0.095973      0.004022      0.016593      0.013700
  26       0.058583      0.002455      0.010128      0.008362
  27       0.046446      0.001946      0.008030      0.006630
  28       0.035374      0.001482      0.006116      0.005049
  29       0.209405      0.008776      0.036205      0.029893
  30       0.000000      0.000000      0.000000      0.000000

  TOTALS      99.999938   100.000015      4.191052

CARBON   BALANCE    11.139190 LB AT/MOLN2.     97.49 PERCENT
HYDROGEN BALANCE    27.872375 LB AT/MOLN2.     97.57 PERCENT
OXYGEN BALANCE       0.466486 LB AT/MOLN2.     87.74 PERCENT

PERCENT O2 REACT      91.1884     PERCENT C4 REACT      10.2782

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
           MOLE PRODUCT PER MOLE N-BUTANE
0.2672   0.0484   0.1874   0.2200   0.3648   0.0945   0.5701   0.4949
           MOLE PRODUCT PER MOLE N-BUTENES
1.4259   0.2587   1.0000   1.1738   1.9465   0.5042   3.0419   2.6410
           MOLE PRODUCT PER MOLE CO
1.0000   0.1814   0.7013   0.8232   1.3650   0.3536   2.1333   1.8521
           MOLE PRODUCT PER MOLE ETHENE
1.8634   0.3381   1.3068   1.5340   2.5437   0.6589   3.9752   3.4513
```

```
RUN NO =  71  SAMPLE NO =  5

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1       0.000000      0.000000      0.000000      0.000000
    2       0.522892      0.021707      0.088924      0.068419
    3      24.087715      1.000000      4.096433      3.151830
    4       2.345620      0.097378      0.398903      0.306919
    5       0.868589      0.036059      0.147715      0.113653
    6       0.789432      0.032773      0.134253      0.103295
    7       0.282398      0.011723      0.048025      0.036951
    8       0.130337      0.005410      0.022165      0.017054
    9       0.471886      0.019590      0.080250      0.061745
   10       0.196301      0.008149      0.033383      0.025685
   11       0.144585      0.006002      0.024588      0.018918
   12       1.298556      0.053909      0.220836      0.169913
   13      61.161201      2.539103     10.401268      8.002822
   14       0.041956      0.001741      0.007135      0.005489
   15       0.020904      0.000867      0.003555      0.002735
   16       0.092742      0.003850      0.015772      0.012135
   17       2.782578      0.115518      0.473214      0.364094
   18       0.687848      0.028555      0.116977      0.090003
   19       2.455324      0.101932      0.417560      0.321274
   20       0.356067      0.014782      0.060554      0.046590
   21       0.159586      0.006625      0.027139      0.020881
   22       0.524400      0.021770      0.089181      0.068616
   23       0.017015      0.000706      0.002893      0.002226
   24       0.153072      0.006354      0.026032      0.020029
   25       0.048136      0.001998      0.008186      0.006298
   26       0.067485      0.002801      0.011476      0.008830
   27       0.031138      0.001292      0.005295      0.004074
   28       0.038567      0.001601      0.006558      0.005046
   29       0.223763      0.009289      0.038053      0.029278
   30       0.000000      0.000000      0.000000      0.000000

 TOTALS   100.000015     99.999969      4.151491

CARBON   BALANCE    11.044004 LB AT/MOLN2.     96.66 PERCENT
HYDROGEN BALANCE    27.565601 LB AT/MOLN2.     96.50 PERCENT
OXYGEN BALANCE       0.461723 LB AT/MOLN2.     86.84 PERCENT

PERCENT O2 REACT     91.8337     PERCENT C4 REACT     11.1076

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.3069    0.0121   0.1888   0.1676   0.3802   0.1606   0.6231   0.3640
            MOLE  PRODUCT  PER MOLE  N-BUTENES
1.6253    0.0642   1.0000   0.8878   2.0137   0.8510   3.3000   1.9281
            MOLE  PRODUCT  PER MOLE  CO
1.0000    0.0395   0.6152   0.5462   1.2389   0.5235   2.0303   1.1862
            MOLE  PRODUCT  PER MOLE  ETHENE
2.9712    0.1174   1.8280   1.6230   3.6813   1.5557   6.0326   3.5247
```

```
RUN NO =  73
REACTOR ENTRANCE CONDITIONS


AIR =    2.30 LB/HR            BUTANE =    9.20 LB/HR
TEMPERATURE =    678.00 DEG F
PRESSURE =  53.72 LB/SQ IN
OXYGEN  = 7.0333 NITROGEN = 26.4589 BUTANE = 66.5076  MOL PCNT
OXY/N = 0.2658 NIT/N   = 1.0000 BUT/N   =  2.5136  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =    9.4559
DENSITY OF GAS MIXTURE =    0.2125 LB/CU FT
GAS VELOCITY =   7.05 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.37 SEC
REYNOLDS NUMBER =    6015
```

```
RUN NO =   73   SAMPLE NO =   1

  PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
     1        0.000000       0.000000       0.000000       0.000000
     2        6.735735       0.255434      24.589363      12.922405
     3       26.369693       1.000000      96.264770      50.589859
     4        0.044222       0.001677       0.161437       0.084840
     5        0.000000       0.000000       0.000000       0.000000
     6        0.011817       0.000448       0.043139       0.022671
     7        0.000000       0.000000       0.000000       0.000000
     8        0.000000       0.000000       0.000000       0.000000
     9        0.538579       0.020424       1.966129       1.033256
    10        0.105647       0.004006       0.385675       0.202683
    11        0.091110       0.003455       0.332607       0.174794
    12        0.021585       0.000818       0.078800       0.041412
    13       65.761993       2.493847     240.069610     126.163375
    14        0.000000       0.000000       0.000000       0.000000
    15        0.000000       0.000000       0.000000       0.000000
    16        0.059945       0.002273       0.218836       0.115004
    17        0.000000       0.000000       0.000000       0.000000
    18        0.036274       0.001375       0.132421       0.069591
    19        0.077554       0.002941       0.283117       0.148786
    20        0.000000       0.000000       0.000000       0.000000
    21        0.000000       0.000000       0.000000       0.000000
    22        0.145901       0.005532       0.532626       0.279910
    23        0.000000       0.000000       0.000000       0.000000
    24        0.000000       0.000000       0.000000       0.000000
    25        0.000000       0.000000       0.000000       0.000000
    26        0.000000       0.000000       0.000000       0.000000
    27        0.000000       0.000000       0.000000       0.000000
    28        0.000000       0.000000       0.000000       0.000000
    29        0.000000       0.000000       0.000000       0.000000
    30        0.000000       0.000000       0.000000       0.000000

  TOTALS     099.999999     099.999999       3.792232

CARBON    BALANCE    10.090005 LB AT/MOLN2.    100.35 PERCENT
HYDROGEN BALANCE     25.173702 LB AT/MOLN2.    100.14 PERCENT
OXYGEN BALANCE        0.526942 LB AT/MOLN2.     99.11 PERCENT

PERCENT O2 REACT       3.9078     PERCENT C4 REACT       0.7863

  CO        CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE PRODUCT PER MOLE N-BUTANE
0.C848    0.1150  0.2162   0.0000   0.1487   0.0695   0.4982   0.0000
            MOLE PRODUCT PER MOLE N-BUTENES
0.3924    0.5319  1.0000   0.0000   0.6881   0.3218   2.3046   0.0000
            MOLE PRODUCT PER MOLE CO
1.0000    1.3555  2.5483   0.0000   1.7537   0.8202   5.8732   0.0000
            MOLE PRODUCT PER MOLE ETHENE
3.7421    5.0727  9.5366   0.0000   6.5627   3.0695  21.9789   0.0000
```

```
RUN NO =   73   SAMPLE NO =   2

PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
  1         0.000000      0.000000       0.000000       0.000000
  2         5.556699      0.212644       3.998744       2.470916
  3        26.131362      1.000000      18.804809      11.619922
  4         0.289617      0.011083       0.208415       0.128785
  5         0.032918      0.001259       0.023688       0.014637
  6         0.094639      0.003621       0.068105       0.042083
  7         0.000000      0.000000       0.000000       0.000000
  8         0.000000      0.000000       0.000000       0.000000
  9         1.250891      0.047869       0.900174       0.556238
 10         0.071657      0.002742       0.051566       0.031864
 11         0.382295      0.014629       0.275109       0.169996
 12         0.417984      0.015995       0.300792       0.185866
 13        63.435317      2.427555      45.649696      28.208000
 14         0.000000      0.000000       0.000000       0.000000
 15         0.000000      0.000000       0.000000       0.000000
 16         0.320952      0.012282       0.230965       0.142719
 17         0.262814      0.010057       0.189128       0.116866
 18         0.032691      0.001251       0.023525       0.014536
 19         0.953552      0.036490       0.686201       0.424019
 20         0.079003      0.003023       0.056853       0.035130
 21         0.080961      0.003098       0.058261       0.036001
 22         0.193152      0.007391       0.138997       0.085889
 23         0.051673      0.001977       0.037185       0.022978
 24         0.095915      0.003670       0.069023       0.042651
 25         0.102211      0.003911       0.073553       0.045450
 26         0.000000      0.000000       0.000000       0.000000
 27         0.000000      0.000000       0.000000       0.000000
 28         0.000000      0.000000       0.000000       0.000000
 29         0.163819      0.006269       0.117888       0.072846
 30         0.000000      0.000000       0.000000       0.000000

  TOTALS   100.000015    100.000015      3.826820

CARBON    BALANCE     10.137680 LB AT/MOLN2.    100.82 PERCENT
HYDROGEN BALANCE      25.203571 LB AT/MOLN2.    100.26 PERCENT
OXYGEN BALANCE         0.538077 LB AT/MOLN2.    101.20 PERCENT

PERCENT O2 REACT     20.0050     PERCENT C4 REACT        3.4237

   CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD    OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
 0.1287   0.1427   0.3558   0.0146   0.5328   0.0923    0.7795   0.1168
            MOLE  PRODUCT  PER MOLE  N-BUTENES
 0.3618   0.4010   1.0000   0.0411   1.4973   0.2594    2.1904   0.3284
            MOLE  PRODUCT  PER MOLE  CO
 1.0000   1.1081   2.7632   0.1136   4.1376   0.7168    6.0527   0.9074
            MOLE  PRODUCT  PER MOLE  ETHENE
 3.0602   3.3913   8.4560   0.3478  12.6620   2.1936   18.5226   2.7769
```

```
RUN NO =  73  SAMPLE NO =  3

PRD NO  MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
  1       0.000000      0.000000      0.000000      0.000000
  2       2.392937      0.089924      0.511229      0.372916
  3      26.610538      1.000000      5.685104      4.146995
  4       1.179711      0.044332      0.252034      0.183846
  5       0.310871      0.011682      0.066414      0.048446
  6       0.556060      0.020896      0.118797      0.086656
  7       0.100980      0.003794      0.021573      0.015736
  8       0.015236      0.000572      0.003255      0.002374
  9       1.587761      0.059666      0.339210      0.247437
 10       0.062563      0.002351      0.013366      0.009749
 11       0.593016      0.022285      0.126692      0.092415
 12       1.217253      0.045743      0.260055      0.189697
 13      60.471794      2.272475     12.919258      9.423944
 14       0.000000      0.000000      0.000000      0.000000
 15       0.000000      0.000000      0.000000      0.000000
 16       0.515825      0.019384      0.110201      0.080386
 17       1.290696      0.048503      0.275745      0.201142
 18       0.102453      0.003850      0.021888      0.015966
 19       1.891610      0.071085      0.404125      0.294789
 20       0.373188      0.014024      0.079728      0.058157
 21       0.107068      0.004023      0.022874      0.016685
 22       0.139964      0.005259      0.029902      0.021812
 23       0.069096      0.002596      0.014761      0.010768
 24       0.100276      0.003768      0.021423      0.015627
 25       0.044567      0.001674      0.009521      0.006945
 26       0.000000      0.000000      0.000000      0.000000
 27       0.000000      0.000000      0.000000      0.000000
 28       0.032750      0.001230      0.006996      0.005103
 29       0.233905      0.008789      0.049971      0.036451
 30       0.000000      0.000000      0.000000      0.000000

TOTALS       99.999908     100.000015      3.757910

CARBON   BALANCE      9.863891 LB AT/MOLN2.     98.10 PERCENT
HYDROGEN BALANCE     24.448135 LB AT/MOLN2.     97.26 PERCENT
OXYGEN BALANCE        0.427755 LB AT/MOLN2.     80.45 PERCENT

PERCENT O2 REACT      66.1712      PERCENT C4 REACT       9.5932

   CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.1838    0.0803   0.2821   0.0665   0.3479   0.0897   0.4823   0.2011
            MOLE  PRODUCT  PER MOLE  N-BUTENES
0.6516    0.2849   1.0000   0.2359   1.2332   0.3181   1.7096   0.7129
            MOLE  PRODUCT  PER MOLE  CO
1.0000    0.4372   1.5345   0.3620   1.8924   0.4881   2.6234   1.0940
            MOLE  PRODUCT  PER MOLE  ETHENE
2.1215    0.9276   3.2555   0.7680   4.0150   1.0357   5.5657   2.3211
```

```
RUN NO =  73   SAMPLE NO =   4

  PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
     1       0.000000      0.000000      0.000000      0.000000
     2       0.298470      0.011151      0.043787      0.031957
     3      26.765254      1.000000      3.926630      2.865784
     4       1.899742      0.070977      0.278704      0.203407
     5       0.640388      0.023926      0.093948      0.068567
     6       0.776641      0.029016      0.113938      0.083155
     7       0.147730      0.005519      0.021672      0.015817
     8       0.045277      0.001691      0.006642      0.004847
     9       0.910947      0.034034      0.133641      0.097536
    10       0.061014      0.002279      0.008951      0.006532
    11       0.320185      0.011962      0.046973      0.034282
    12       1.585602      0.059241      0.232617      0.169772
    13      57.937927      2.164669      8.499856      6.203474
    14       0.040361      0.001507      0.005921      0.004321
    15       0.025413      0.000949      0.003728      0.002721
    16       0.480291      0.017944      0.070461      0.051425
    17       2.664578      0.099553      0.390910      0.285299
    18       0.179289      0.006698      0.026302      0.019196
    19       3.082465      0.115166      0.452217      0.330042
    20       0.732210      0.027356      0.107419      0.078398
    21       0.119944      0.004481      0.017596      0.012842
    22       0.377981      0.014122      0.055452      0.040470
    23       0.179093      0.006691      0.026274      0.019175
    24       0.203561      0.007605      0.029863      0.021795
    25       0.080566      0.003010      0.011819      0.008626
    26       0.045129      0.001686      0.006620      0.004832
    27       0.033384      0.001247      0.004897      0.003574
    28       0.103811      0.003878      0.015229      0.011115
    29       0.262953      0.009824      0.038576      0.028154
    30       0.000000      0.000000      0.000000      0.000000

  TOTALS    99.999969    100.000061      3.736191

CARBON    BALANCE      9.586923 LB AT/MOLN2.     95.34 PERCENT
HYDROGEN BALANCE      23.862388 LB AT/MOLN2.     94.93 PERCENT
OXYGEN BALANCE         0.430492 LB AT/MOLN2.     80.97 PERCENT

PERCENT O2 REACT      95.8049     PERCENT C4 REACT     13.8821

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.2034   0.0514   0.2040   0.0892   0.3758   0.1229   0.5782   0.2852
           MOLE  PRODUCT  PER MOLE  N-BUTENES
0.9968   0.2520   1.0000   0.4372   1.8420   0.6026   2.8336   1.3981
           MOLE  PRODUCT  PER MOLE  CO
1.0000   0.2528   1.0031   0.4386   1.8478   0.6045   2.8426   1.4026
           MOLE  PRODUCT  PER MOLE  ETHENE
2.4461   0.6184   2.4538   1.0730   4.5200   1.4787   6.9535   3.4308
```

```
RUN NO =   73   SAMPLE NO =   5

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1       0.000000       0.000000       0.000000       0.000000
    2       0.426611       0.016119       0.064556       0.055832
    3      26.464939       1.000000       4.004760       3.463556
    4       3.130710       0.118296       0.473749       0.409726
    5       0.608912       0.023008       0.092142       0.079690
    6       0.747669       0.028251       0.113139       0.097850
    7       0.178775       0.006755       0.027052       0.023396
    8       0.081326       0.003072       0.012306       0.010643
    9       0.809831       0.030600       0.122546       0.105985
   10       0.085166       0.003218       0.012887       0.011146
   11       0.202320       0.007644       0.030615       0.026478
   12       1.316199       0.049733       0.199171       0.172255
   13      58.881668       2.224893       8.910165       7.706042
   14       0.036950       0.001396       0.005591       0.004835
   15       0.018475       0.000698       0.002795       0.002417
   16       0.472850       0.017867       0.071553       0.061883
   17       2.531255       0.095645       0.383037       0.331273
   18       0.127096       0.004802       0.019232       0.016633
   19       2.191590       0.082811       0.331638       0.286820
   20       0.556666       0.021034       0.084236       0.072852
   21       0.089005       0.003363       0.013468       0.011648
   22       0.316660       0.011965       0.047918       0.041442
   23       0.124063       0.004687       0.018773       0.016236
   24       0.153979       0.005818       0.023300       0.020151
   25       0.053347       0.002015       0.008072       0.006981
   26       0.075747       0.002862       0.011462       0.009913
   27       0.019706       0.000744       0.002982       0.002579
   28       0.064150       0.002423       0.009707       0.008395
   29       0.234533       0.008862       0.035490       0.030694
   30       0.000000       0.000000       0.000000       0.000000

 TOTALS    99.999908     100.000076       3.778587

CARBON   BALANCE       9.738262 LB AT/MOLN2.     96.85 PERCENT
HYDROGEN BALANCE      24.119789 LB AT/MOLN2.     95.95 PERCENT
OXYGEN BALANCE         0.433306 LB AT/MOLN2.     81.50 PERCENT

PERCENT O2 REACT     93.9358     PERCENT C4 REACT     11.4862

  CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.4097   0.0618   0.1987   0.1137   0.3390   0.1122   0.5243   0.3312
          MOLE  PRODUCT  PER MOLE  N-BUTENES
2.0616   0.3113   1.0000   0.5722   1.7061   0.5646   2.6384   1.6669
          MOLE  PRODUCT  PER MOLE  CO
1.0000   0.1510   0.4850   0.2775   0.8275   0.2738   1.2797   0.8085
          MOLE  PRODUCT  PER MOLE  ETHENE
4.1872   0.6324   2.0310   1.1622   3.4652   1.1468   5.3587   3.3855
```

```
RUN NO =  75
REACTOR ENTRANCE CONDITIONS


AIR =   2.30 LB/HR            BUTANE =   8.20 LB/HR
TEMPERATURE =   655.00 DEG F
PRESSURE =  51.35 LB/SQ IN
OXYGEN = 7.5814 NITROGEN = 28.5207 BUTANE = 63.8977  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  2.2403  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   8.4281
DENSITY OF GAS MIXTURE =   0.2041 LB/CU FT
GAS VELOCITY =   6.70 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.44 SEC
REYNOLDS NUMBER =    5492
```

```
RUN NO =   75   SAMPLE NO =   1

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1        0.000000       0.000000       0.000000       0.000000
    2        7.120763       0.251145      17.110580      49.842842
    3       28.353195       1.000000      68.130279     198.462402
    4        0.056273       0.001984       0.135220       0.393894
    5        0.000000       0.000000       0.000000       0.000000
    6        0.001870       0.000065       0.004494       0.013093
    7        0.000000       0.000000       0.000000       0.000000
    8        0.000000       0.000000       0.000000       0.000000
    9        0.557253       0.019653       1.339030       3.900575
   10        0.070625       0.002490       0.169707       0.494354
   11        0.077118       0.002719       0.185308       0.539800
   12        0.006577       0.000231       0.015805       0.046039
   13       63.379486       2.235356     152.295410     443.634094
   14        0.000000       0.000000       0.000000       0.000000
   15        0.000000       0.000000       0.000000       0.000000
   16        0.323609       0.011413       0.777605       2.265152
   17        0.000000       0.000000       0.000000       0.000000
   18        0.000000       0.000000       0.000000       0.000000
   19        0.053254       0.001878       0.127965       0.372762
   20        0.000000       0.000000       0.000000       0.000000
   21        0.000000       0.000000       0.000000       0.000000
   22        0.000000       0.000000       0.000000       0.000000
   23        0.000000       0.000000       0.000000       0.000000
   24        0.000000       0.000000       0.000000       0.000000
   25        0.000000       0.000000       0.000000       0.000000
   26        0.000000       0.000000       0.000000       0.000000
   27        0.000000       0.000000       0.000000       0.000000
   28        0.000000       0.000000       0.000000       0.000000
   29        0.000000       0.000000       0.000000       0.000000
   30        0.000000       0.000000       0.000000       0.000000

 TOTALS     99.999984     100.000015       3.526938

CARBON   BALANCE      9.037563 LB AT/MOLN2.    100.84 PERCENT
HYDROGEN BALANCE     22.527782 LB AT/MOLN2.    100.55 PERCENT
OXYGEN BALANCE        0.528979 LB AT/MOLN2.     99.49 PERCENT

PERCENT O2 REACT      5.5216     PERCENT C4 REACT      0.2249

   CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
 0.3938   2.2651   0.5858   0.0000   0.3727   0.0000   0.3727   0.0000
           MOLE  PRODUCT  PER MOLE  N-BUTENES
 0.6723   3.8665   1.0000   0.0000   0.6362   0.0000   0.6362   0.0000
           MOLE  PRODUCT  PER MOLE  CO
 1.0000   5.7506   1.4873   0.0000   0.9463   0.0000   0.9463   0.0000
           MOLE  PRODUCT  PER MOLE  ETHENE
30.0835173.0000  44.7432   0.0000  28.4695   0.0000  28.4695   0.0000
```

```
RUN NO =  75   SAMPLE NO =   2
                                                           MOLS/MBUT  R
 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R
   1        0.000000       0.000000       0.000000        0.000000
   2        6.801396       0.238518       8.735589        5.877558
   3       28.515167       1.000000      36.624359       24.641937
   4        0.084489       0.002962       0.108516        0.073013
   5        0.000000       0.000000       0.000000        0.000000
   6        0.015748       0.000552       0.020227        0.013609
   7        0.000000       0.000000       0.000000        0.000000
   8        0.000000       0.000000       0.000000        0.000000
   9        0.798050       0.027986       1.025001        0.689650
  10        0.066332       0.002326       0.085195        0.057322
  11        0.289788       0.010162       0.372198        0.250426
  12        0.045770       0.001605       0.058787        0.039553
  13       62.728050       2.199813      80.566757       54.207664
  14        0.000000       0.000000       0.000000        0.000000
  15        0.000000       0.000000       0.000000        0.000000
  16        0.128227       0.004496       0.164693        0.110810
  17        0.032321       0.001133       0.041513        0.027931
  18        0.000000       0.000000       0.000000        0.000000
  19        0.252670       0.008860       0.324525        0.218350
  20        0.000000       0.000000       0.000000        0.000000
  21        0.000000       0.000000       0.000000        0.000000
  22        0.089461       0.003137       0.114902        0.077309
  23        0.072817       0.002553       0.093525        0.062926
  24        0.046967       0.001647       0.060323        0.040587
  25        0.000000       0.000000       0.000000        0.000000
  26        0.032825       0.001151       0.042160        0.028366
  27        0.000000       0.000000       0.000000        0.000000
  28        0.000000       0.000000       0.000000        0.000000
  29        0.000000       0.000000       0.000000        0.000000
  30        0.000000       0.000000       0.000000        0.000000

 TOTALS     99.999969     100.000045       3.506906

CARBON    BALANCE     8.979339 LB  AT/MOLN2.    100.19 PERCENT
HYDROGEN BALANCE     22.370330 LB  AT/MOLN2.     99.84 PERCENT
OXYGEN BALANCE        0.507477 LB  AT/MOLN2.     95.45 PERCENT

PERCENT O2 REACT      10.2715      PERCENT C4 REACT       1.8113

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE PRODUCT  PER MOLE  N-BUTANE
0.0730   0.1108   0.2899   0.0000   0.2467   0.0405   0.4275   0.0279
           MOLE PRODUCT  PER MOLE  N-BUTENES
0.2517   0.3821   1.0000   0.0000   0.8508   0.1399   1.4743   0.0963
           MOLE PRODUCT  PER MOLE  CO
1.0000   1.5176   3.9716   0.0000   3.3790   0.5558   5.8556   0.3825
           MOLE PRODUCT  PER MOLE  ETHENE
5.3647   8.1420  21.3068   0.0000  18.1280   2.9822  31.4143   2.0523
```

```
  RUN NO =   75   SAMPLE NO =   3

   PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
      1        0.000000      0.000000      0.000000      0.000000
      2        5.997882      0.210000      3.761904      4.633078
      3       28.561347      1.000000     17.913833     22.062282
      4        0.301833      0.010567      0.189311      0.233151
      5        0.038826      0.001359      0.024352      0.029991
      6        0.069160      0.002421      0.043377      0.053423
      7        0.008222      0.000287      0.005156      0.006351
      8        0.000000      0.000000      0.000000      0.000000
      9        0.525550      0.018400      0.329628      0.405962
     10        0.061365      0.002148      0.038488      0.047401
     11        0.188870      0.006612      0.118460      0.145893
     12        0.178784      0.006259      0.112134      0.138102
     13       62.694122      2.195068     39.322090     48.428215
     14        0.039936      0.001398      0.025048      0.030848
     15        0.037440      0.001310      0.023482      0.028920
     16        0.212941      0.007455      0.133558      0.164487
     17        0.025362      0.000888      0.015907      0.019591
     18        0.030726      0.001075      0.019272      0.023735
     19        0.660023      0.023108      0.413970      0.509837
     20        0.061279      0.002145      0.038434      0.047335
     21        0.040925      0.001432      0.025668      0.031613
     22        0.059096      0.002069      0.037065      0.045649
     23        0.040023      0.001401      0.025102      0.030916
     24        0.047502      0.001663      0.029793      0.036693
     25        0.000000      0.000000      0.000000      0.000000
     26        0.000000      0.000000      0.000000      0.000000
     27        0.118918      0.004163      0.074586      0.091858
     28        0.000000      0.000000      0.000000      0.000000
     29        0.000000      0.000000      0.000000      0.000000
     30        0.000000      0.000000      0.000000      0.000000

   TOTALS      99.999969    100.000015      3.501236

CARBON    BALANCE      8.993825 LB AT/MOLN2.     100.35 PERCENT
HYDROGEN BALANCE      22.405612 LB AT/MOLN2.     100.00 PERCENT
OXYGEN BALANCE         0.483427 LB AT/MOLN2.      90.93 PERCENT

PERCENT O2 REACT     21.0000     PERCENT C4 REACT      2.0231

  CO       CO2    BUTEN    PARFIN  ALCOHL  ALDHYD  OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.2331  0.1644  0.2839   0.0363   0.5414  0.1996  0.8176  0.0195
          MOLE PRODUCT PER MOLE N-BUTENES
0.8209  0.5791  1.0000   0.1279   1.9065  0.7029  2.8790  0.0689
          MOLE PRODUCT PER MOLE CO
1.0000  0.7054  1.2180   0.1558   2.3223  0.8561  3.5068  0.0840
          MOLE PRODUCT PER MOLE ETHENE
4.3642  3.0789  5.3159   0.6802  10.1351 3.7366 15.3049  0.3667
```

```
  RUN NO =  75  SAMPLE NO =  4

   PRD NO  MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R  MOLS/MBUT R
     1       0.000000      0.000000      0.000000      0.000000
     2       3.221381      0.110198      0.708100      0.526986
     3      29.232658      1.000000      6.425713      4.782177
     4       0.904475      0.030940      0.198815      0.147963
     5       0.207886      0.007111      0.045696      0.034008
     6       0.228070      0.007801      0.050132      0.037310
     7       0.066546      0.002276      0.014627      0.010886
     8       0.000000      0.000000      0.000000      0.000000
     9       0.766624      0.026224      0.168513      0.125412
    10       0.050939      0.001742      0.011197      0.008333
    11       0.277616      0.009496      0.061023      0.045415
    12       0.724510      0.024784      0.159256      0.118522
    13      59.379867      2.031285     13.052453      9.713964
    14       0.000000      0.000000      0.000000      0.000000
    15       0.000000      0.000000      0.000000      0.000000
    16       0.287354      0.009829      0.063164      0.047008
    17       1.341826      0.045901      0.294950      0.219509
    18       0.066016      0.002258      0.014511      0.010799
    19       2.322640      0.079453      0.510546      0.379961
    20       0.194223      0.006644      0.042692      0.031773
    21       0.078958      0.002701      0.017356      0.012916
    22       0.070001      0.002394      0.015387      0.011451
    23       0.046546      0.001592      0.010231      0.007614
    24       0.091373      0.003125      0.020085      0.014947
    25       0.058413      0.001998      0.012840      0.009555
    26       0.000000      0.000000      0.000000      0.000000
    27       0.099009      0.003386      0.021763      0.016196
    28       0.000000      0.000000      0.000000      0.000000
    29       0.283168      0.009686      0.062244      0.046323
    30       0.000000      0.000000      0.000000      0.000000

   TOTALS   099.999999    99.999984      3.420831

CARBON   BALANCE     8.593570 LB AT/MOLN2.     95.89 PERCENT
HYDROGEN BALANCE    21.465919 LB AT/MOLN2.     95.81 PERCENT
OXYGEN BALANCE       0.430139 LB AT/MOLN2.     80.90 PERCENT

PERCENT O2 REACT     58.5445     PERCENT C4 REACT      9.3336

  CO       CO2    BUTEN    PARFIN  ALCOHL  ALDHYD   OXYGCO    WATER
           MOLE PRODUCT PER MOLE N-BUTANE
0.1479  0.0470   0.1639   0.0448  0.4392  0.0737   0.5415   0.2195
           MOLE PRODUCT PER MOLE N-BUTENES
0.9025  0.2867   1.0000   0.2738  2.6790  0.4496   3.3033   1.3389
           MOLE PRODUCT PER MOLE CO
1.0000  0.3177   1.1079   0.3034  2.9683  0.4982   3.6599   1.4835
           MOLE PRODUCT PER MOLE ETHENE
3.9657  1.2599   4.3939   1.2032 11.7716  1.9758 14.5145   5.8833
```

```
RUN NO =  77
REACTOR ENTRANCE CONDITIONS


AIR =    2.95 LB/HR            BUTANE =    9.20 LB/HR
TEMPERATURE =   650.00 DEG F
PRESSURE =  53.50 LB/SQ IN
OXYGEN = 8.2410 NITROGEN = 31.0020 BUTANE = 60.7568  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  1.9597  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   7.3724
DENSITY OF GAS MIXTURE =   0.2094 LB/CU FT
GAS VELOCITY =   7.56 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.27 SEC
REYNOLDS NUMBER =    6245
```

```
RUN NO =  77  SAMPLE NO =  1

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1       0.000000       0.000000       0.000000       0.000000
    2       7.112522       0.229974       6.415313      26.060001
    3      30.927375       1.000000      27.895706     113.316696
    4       0.119993       0.003879       0.108231       0.439651
    5       0.020677       0.000668       0.018650       0.075759
    6       0.029383       0.000950       0.026502       0.107658
    7       0.003771       0.000121       0.003401       0.013817
    8       0.000000       0.000000       0.000000       0.000000
    9       0.689704       0.022300       0.622096       2.527051
   10       0.057332       0.001853       0.051712       0.210065
   11       0.034086       0.001102       0.030745       0.124891
   12       0.089453       0.002892       0.080685       0.327755
   13      60.337524       1.950942      54.422904     221.074310
   14       0.000000       0.000000       0.000000       0.000000
   15       0.000000       0.000000       0.000000       0.000000
   16       0.100540       0.003250       0.090685       0.368377
   17       0.068359       0.002210       0.061658       0.250466
   18       0.020264       0.000655       0.018277       0.074247
   19       0.310263       0.010032       0.279850       1.136794
   20       0.023227       0.000751       0.020950       0.085105
   21       0.028877       0.000933       0.026047       0.105806
   22       0.000000       0.000000       0.000000       0.000000
   23       0.000000       0.000000       0.000000       0.000000
   24       0.026711       0.000863       0.024093       0.097871
   25       0.000000       0.000000       0.000000       0.000000
   26       0.000000       0.000000       0.000000       0.000000
   27       0.000000       0.000000       0.000000       0.000000
   28       0.000000       0.000000       0.000000       0.000000
   29       0.000000       0.000000       0.000000       0.000000
   30       0.000000       0.000000       0.000000       0.000000

TOTALS    099.999999     099.999999       3.233381

CARBON   BALANCE      7.920653 LB AT/MOLN2.    101.04 PERCENT
HYDROGEN BALANCE     19.760559 LB AT/MOLN2.    100.83 PERCENT
OXYGEN BALANCE        0.485777 LB AT/MOLN2.     91.37 PERCENT

PERCENT O2 REACT     13.4856     PERCENT C4 REACT      0.4502

  CO       CO2    BUTEN   PARFIN   ALCOHL  ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE N-BUTANE
0.4396   0.3683   0.4526   0.0895   1.2426  0.2572   1.4998   0.2504
           MOLE  PRODUCT  PER MOLE N-BUTENES
0.9712   0.8138   1.0000   0.1978   2.7451  0.5682   3.3134   0.5533
           MOLE  PRODUCT  PER MOLE CO
1.0000   0.8378   1.0295   0.2037   2.8263  0.5850   3.4113   0.5696
           MOLE  PRODUCT  PER MOLE ETHENE
4.0837   3.4217   4.2044   0.8320 11.5420  2.3892 13.9313   2.3264
```

```
RUN NO =   77   SAMPLE NO =   2

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1       0.000000       0.000000       0.000000       0.000000
    2       5.410458       0.177373       2.005373       1.800372
    3      30.503177       1.000000      11.305929      10.150171
    4       0.363894       0.011929       0.134876       0.121088
    5       0.407239       0.013350       0.150942       0.135512
    6       0.413784       0.013565       0.153368       0.137689
    7       0.113274       0.003713       0.041984       0.037692
    8       0.008592       0.000281       0.003184       0.002859
    9       1.157999       0.037963       0.429209       0.385333
   10       0.037460       0.001228       0.013884       0.012465
   11       0.201299       0.006599       0.074611       0.066984
   12       0.677830       0.022221       0.251236       0.225553
   13      56.773933       1.861246      21.043117      18.891967
   14       0.013297       0.000435       0.004928       0.004424
   15       0.012466       0.000408       0.004620       0.004148
   16       0.354879       0.011634       0.131535       0.118089
   17       1.196382       0.039221       0.443436       0.398105
   18       0.040924       0.001341       0.015168       0.013617
   19       1.571241       0.051510       0.582376       0.522842
   20       0.344003       0.011277       0.127503       0.114469
   21       0.022462       0.000736       0.008325       0.007474
   22       0.022997       0.000753       0.008523       0.007652
   23       0.034500       0.001131       0.012787       0.011480
   24       0.077884       0.002553       0.028867       0.025916
   25       0.059340       0.001945       0.021994       0.019746
   26       0.005352       0.000175       0.001983       0.001781
   27       0.003368       0.000110       0.001248       0.001120
   28       0.005276       0.000172       0.001955       0.001755
   29       0.166843       0.005469       0.061840       0.055518
   30       0.000000       0.000000       0.000000       0.000000

TOTALS     99.999954     100.000030       3.278346

CARBON    BALANCE      7.874156 LB AT/MOLN2.    100.44 PERCENT
HYDROGEN BALANCE      19.656898 LB AT/MOLN2.    100.30 PERCENT
OXYGEN BALANCE         0.506345 LB AT/MOLN2.     95.24 PERCENT

PERCENT O2 REACT      33.2737     PERCENT C4 REACT       5.0271

  CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT  PER MOLE  N-BUTANE
0.1210   0.1180   0.2925   0.1760   0.5876   0.1551   0.7833   0.3981
           MOLE  PRODUCT  PER MOLE  N-BUTENES
0.4139   0.4036   1.0000   0.6018   2.0086   0.5302   2.6778   1.3608
           MOLE  PRODUCT  PER MOLE  CO
1.0000   0.9752   2.4158   1.4540   4.8527   1.2810   6.4694   3.2877
           MOLE  PRODUCT  PER MOLE  ETHENE
0.8794   0.8576   2.1246   1.2786   4.2676   1.1266   5.6894   2.8913
```

```
RUN NO =   77   SAMPLE NO =   3

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
     1       0.060226      0.002004      0.009468      0.011033
     2       1.624380      0.054073      0.255362      0.297591
     3      30.040496      1.000000      4.722557      5.503505
     4       1.953944      0.065043      0.307172      0.357968
     5       0.840775      0.027988      0.132175      0.154032
     6       0.880711      0.029317      0.138453      0.161348
     7       0.267069      0.008890      0.041985      0.048927
     8       0.055879      0.001860      0.008784      0.010237
     9       1.076191      0.035824      0.169184      0.197161
    10       0.043310      0.001441      0.006808      0.007934
    11       0.341674      0.011373      0.053713      0.062595
    12       1.398424      0.046551      0.219841      0.256195
    13      53.413948      1.778064      8.397010      9.785589
    14       0.035552      0.001183      0.005589      0.006513
    15       0.018833      0.000626      0.002960      0.003450
    16       0.508668      0.016932      0.079965      0.093189
    17       2.935661      0.097723      0.461504      0.537821
    18       0.171170      0.005697      0.026909      0.031358
    19       2.821086      0.093909      0.443492      0.516831
    20       0.672035      0.022370      0.105648      0.123118
    21       0.048303      0.001607      0.007593      0.008849
    22       0.015727      0.000523      0.002472      0.002881
    23       0.066988      0.002229      0.010530      0.012272
    24       0.190057      0.006326      0.029878      0.034819
    25       0.071886      0.002392      0.011300      0.013169
    26       0.027847      0.000927      0.004377      0.005101
    27       0.038331      0.001276      0.006026      0.007022
    28       0.021372      0.000711      0.003359      0.003915
    29       0.353645      0.011772      0.055595      0.064788
    30       0.005986      0.000199      0.000941      0.001096
 TOTALS    099.999999    100.000030      3.328840

CARBON   BALANCE       7.898208 LB AT/MOLN2.
HYDROGEN BALANCE      19.689365 LB AT/MOLN2.     100.75 PERCENT
OXYGEN BALANCE         0.454723 LB AT/MOLN2.     100.46 PERCENT
                                                  85.53 PERCENT
PERCENT O2 REACT      79.6582     PERCENT C4 REACT       9.2716

  CO       CO2     BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
          MOLE PRODUCT PER MOLE N-BUTANE
0.3579   0.0931   0.3187   0.2242   0.5955   0.1963   0.8252   0.5378
          MOLE PRODUCT PER MOLE N-BUTENES
1.1228   0.2923   1.0000   0.7033   1.8682   0.6158   2.5886   1.6870
          MOLE PRODUCT PER MOLE CO
1.0000   0.2603   0.8905   0.6263   1.6637   0.5484   2.3053   1.5024
          MOLE PRODUCT PER MOLE ETHENE
2.2185   0.5775   1.9757   1.3897   3.6911   1.2167   5.1145   3.3332
```

```
RUN NO =   77   SAMPLE NO =   4

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1       0.303068       0.010071       0.040560       0.038784
    2       0.527292       0.017522       0.070568       0.067479
    3      30.092658       1.000000       4.027379       3.851037
    4       2.625919       0.087261       0.351433       0.336045
    5       1.523777       0.050636       0.203931       0.195001
    6       1.351357       0.044906       0.180855       0.172936
    7       0.481117       0.015987       0.064389       0.061569
    8       0.124086       0.004123       0.016606       0.015879
    9       0.740390       0.024603       0.099088       0.094749
   10       0.042662       0.001417       0.005709       0.005459
   11       0.326106       0.010836       0.043643       0.041732
   12       1.596063       0.053038       0.213605       0.204252
   13      51.160430       1.700096       6.846933       6.547137
   14       0.028921       0.000961       0.003870       0.003701
   15       0.018972       0.000630       0.002539       0.002427
   16       0.531432       0.017659       0.071123       0.068008
   17       4.071214       0.135289       0.544861       0.521004
   18       0.166707       0.005539       0.022310       0.021333
   19       2.753183       0.091490       0.368465       0.352332
   20       0.764734       0.025412       0.102346       0.097865
   21       0.064096       0.002129       0.008578       0.008202
   22       0.023936       0.000795       0.003203       0.003063
   23       0.064407       0.002140       0.008619       0.008242
   24       0.131187       0.004359       0.017557       0.016788
   25       0.096174       0.003195       0.012871       0.012307
   26       0.060402       0.002007       0.008083       0.007729
   27       0.037018       0.001230       0.004954       0.004737
   28       0.000000       0.000000       0.000000       0.000000
   29       0.292803       0.009730       0.039186       0.037470
   30       0.000000       0.000000       0.000000       0.000000

 TOTALS    99.999938     099.999999      3.323069

CARBON   BALANCE      7.664731 LB AT/MOLN2.     97.77 PERCENT
HYDROGEN BALANCE     19.168750 LB AT/MOLN2.     97.81 PERCENT
OXYGEN BALANCE        0.440945 LB AT/MOLN2.     82.93 PERCENT

PERCENT O2 REACT      93.4082     PERCENT C4 REACT      13.2500

   CO      CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.3360   0.0680   0.2459   0.3112   0.4057   0.1407   0.5700   0.5210
          MOLE  PRODUCT  PER MOLE  N-BUTENES
1.3661   0.2764   1.0000   1.2652   1.6494   0.5720   2.3175   2.1180
          MOLE  PRODUCT  PER MOLE  CO
1.0000   0.2023   0.7319   0.9261   1.2073   0.4187   1.6964   1.5503
          MOLE  PRODUCT  PER MOLE  ETHENE
1.9431   0.3932   1.4223   1.7997   2.3461   0.8137   3.2964   3.0126
```

```
RUN NO =  80
REACTOR ENTRANCE CONDITIONS


AIR =   3.20 LB/HR            BUTANE =   9.20 LB/HR
TEMPERATURE =   625.00 DEG F
PRESSURE =  53.50 LB/SQ IN
OXYGEN = 8.6517 NITROGEN = 32.5469 BUTANE = 58.8013  MOL PCNT
OXY/N = 0.2658 NIT/N  = 1.0000 BUT/N  =  1.8066  MOLS/MN2
BUTANE TO OXYGEN MOLAR RATIO =   6.7964
DENSITY OF GAS MIXTURE =   0.2116 LB/CU FT
GAS VELOCITY =   7.63 FT/SEC
RESIDENCE TIME BASED ON ENTRANCE CONDITIONS  =  1.26 SEC
REYNOLDS NUMBER =    6412
```

```
RUN NO =   80   SAMPLE NO =   1

 PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
    1        0.000000       0.000000       0.000000       0.000000
    2        5.578352       0.172038       1.834405       2.241549
    3       32.425033       1.000000      10.662765      13.029350
    4        0.299308       0.009230       0.098425       0.120270
    5        0.075772       0.002336       0.024917       0.030447
    6        0.026229       0.000808       0.008625       0.010539
    7        0.001600       0.000049       0.000526       0.000642
    8        0.000000       0.000000       0.000000       0.000000
    9        1.258252       0.038804       0.413768       0.505603
   10        0.162634       0.005015       0.053481       0.065351
   11        0.323258       0.009969       0.106301       0.129895
   12        0.450027       0.013879       0.147988       0.180834
   13       56.092391       1.729910      18.445629      22.539604
   14        0.000000       0.000000       0.000000       0.000000
   15        0.000000       0.000000       0.000000       0.000000
   16        2.312039       0.071304       0.760299       0.929046
   17        0.085737       0.002644       0.028194       0.034452
   18        0.075571       0.002330       0.024851       0.030366
   19        0.154333       0.004759       0.050751       0.062015
   20        0.351409       0.010837       0.115558       0.141206
   21        0.000000       0.000000       0.000000       0.000000
   22        0.328119       0.010119       0.107900       0.131848
   23        0.000000       0.000000       0.000000       0.000000
   24        0.000000       0.000000       0.000000       0.000000
   25        0.000000       0.000000       0.000000       0.000000
   26        0.000000       0.000000       0.000000       0.000000
   27        0.000000       0.000000       0.000000       0.000000
   28        0.000000       0.000000       0.000000       0.000000
   29        0.000000       0.000000       0.000000       0.000000
   30        0.000000       0.000000       0.000000       0.000000

 TOTALS     99.999969      99.999954       3.084036

CARBON   BALANCE      7.285101 LB AT/MOLN2.    100.80 PERCENT
HYDROGEN BALANCE     17.898559 LB AT/MOLN2.     99.06 PERCENT
OXYGEN BALANCE        0.526607 LB AT/MOLN2.     99.05 PERCENT

PERCENT O2 REACT     35.2807     PERCENT C4 REACT      4.2481

   CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE PRODUCT PER MOLE N-BUTANE
 0.1202   0.9290   0.3107   0.0310   0.0620   0.1715   0.3654   0.0344
           MOLE PRODUCT PER MOLE N-BUTENES
 0.3870   2.9898   1.0000   0.1000   0.1995   0.5521   1.1760   0.1108
           MOLE PRODUCT PER MOLE CO
 1.0000   7.7246   2.5835   0.2585   0.5156   1.4265   3.0384   0.2864
           MOLE PRODUCT PER MOLE ETHENE
11.4113  88.1481  29.4820   2.9498   5.8840  16.2789  34.6728   3.2688
```

```
RUN NO =  80  SAMPLE NO =  2

 PRD NO   MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1       1.251537     0.040573      0.186835      0.213007
    2       1.500915     0.048658      0.224063      0.255451
    3      30.845878     1.000000      4.604810      5.249876
    4       2.758574     0.089430      0.411812      0.469501
    5       0.773106     0.025063      0.115412      0.131580
    6       0.940264     0.030482      0.140366      0.160030
    7       0.174041     0.005642      0.025981      0.029621
    8       0.000000     0.000000      0.000000      0.000000
    9       1.377064     0.044643      0.205574      0.234372
   10       0.085617     0.002775      0.012781      0.014571
   11       0.403025     0.013065      0.060165      0.068593
   12       1.661863     0.053876      0.248090      0.282844
   13      49.852470     1.616179      7.442198      8.484741
   14       0.004537     0.000147      0.000677      0.000772
   15       0.005492     0.000178      0.000819      0.000934
   16       1.081304     0.035055      0.161421      0.184034
   17       3.068700     0.099484      0.458109      0.522283
   18       0.169463     0.005493      0.025298      0.028842
   19       2.062552     0.066866      0.307906      0.351040
   20       0.908468     0.029451      0.135620      0.154618
   21       0.000000     0.000000      0.000000      0.000000
   22       0.488200     0.015827      0.072880      0.083090
   23       0.062975     0.002041      0.009401      0.010718
   24       0.147433     0.004779      0.022009      0.025092
   25       0.063624     0.002062      0.009498      0.010828
   26       0.011507     0.000373      0.001717      0.001958
   27       0.012480     0.000404      0.001863      0.002124
   28       0.000000     0.000000      0.000000      0.000000
   29       0.289041     0.009370      0.043149      0.049193
   30       0.000000     0.000000      0.000000      0.000000

TOTALS     99.999954    99.999984      3.241924

CARBON   BALANCE     7.330579 LB AT/MOLN2.    101.43 PERCENT
HYDROGEN BALANCE    18.145484 LB AT/MOLN2.    100.43 PERCENT
OXYGEN BALANCE       0.493014 LB AT/MOLN2.     92.73 PERCENT

PERCENT O2 REACT     81.6951     PERCENT C4 REACT     10.5432

  CO       CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO   WATER
          MOLE  PRODUCT  PER MOLE  N-BUTANE
0.4695   0.1840   0.3514   0.3742   0.4021   0.2106   0.7175   0.5222
          MOLE  PRODUCT  PER MOLE  N-BUTENES
1.3359   0.5236   1.0000   1.0647   1.1444   0.5994   2.0416   1.4861
          MOLE  PRODUCT  PER MOLE  CO
1.0000   0.3919   0.7485   0.7970   0.8566   0.4487   1.5282   1.1124
          MOLE  PRODUCT  PER MOLE  ETHENE
2.9338   1.1499   2.1960   2.3383   2.5132   1.3164   4.4835   3.2636
```

```
RUN NO =  80  SAMPLE NO =  3

 PRD NO  MOL PERCENT   MOLS/MOL N2   MOLS/MOXY R   MOLS/MBUT R
    1      1.279242     0.040573      0.161284      0.160842
    2      0.449476     0.014256      0.056669      0.056513
    3     31.528709     1.000000      3.975090      3.964198
    4      3.268219     0.103658      0.412051      0.410922
    5      0.810691     0.025712      0.102210      0.101930
    6      1.117298     0.035437      0.140867      0.140481
    7      0.234770     0.007446      0.029599      0.029518
    8      0.000000     0.000000      0.000000      0.000000
    9      1.284831     0.040751      0.161989      0.161545
   10      0.054147     0.001717      0.006826      0.006808
   11      0.410127     0.013008      0.051708      0.051566
   12      2.047757     0.064948      0.258177      0.257470
   13     49.008300     1.554402      6.178888      6.161958
   14      0.012115     0.000384      0.001527      0.001523
   15      0.009312     0.000295      0.001174      0.001170
   16      0.680772     0.021592      0.085830      0.085595
   17      3.588767     0.113825      0.452466      0.451226
   18      0.121281     0.003846      0.015290      0.015249
   19      2.232441     0.070806      0.281462      0.280691
   20      0.809787     0.025684      0.102096      0.101816
   21      0.000000     0.000000      0.000000      0.000000
   22      0.513560     0.016288      0.064748      0.064571
   23      0.047278     0.001499      0.005960      0.005944
   24      0.135634     0.004301      0.017100      0.017053
   25      0.048329     0.001532      0.006093      0.006076
   26      0.020217     0.000641      0.002549      0.002542
   27      0.019891     0.000630      0.002507      0.002501
   28      0.056091     0.001779      0.007071      0.007052
   29      0.211103     0.006695      0.026615      0.026542
   30      0.000000     0.000000      0.000000      0.000000

 TOTALS    99.999938   100.000030     3.171712

CARBON   BALANCE     7.119027 LB AT/MOLN2.    98.51 PERCENT
HYDROGEN BALANCE    17.634323 LB AT/MOLN2.    97.60 PERCENT
OXYGEN  BALANCE      0.422887 LB AT/MOLN2.    79.54 PERCENT

PERCENT O2 REACT     94.6369    PERCENT C4 REACT     13.9626

  CO       CO2    BUTEN   PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
           MOLE  PRODUCT PER MOLE N-BUTANE
0.4109   0.0855   0.3090  0.2922   0.3097   0.1366   0.5300   0.4512
           MOLE  PRODUCT PER MOLE N-BUTENES
1.3296   0.2769   1.0000  0.9458   1.0023   0.4420   1.7151   1.4601
           MOLE  PRODUCT PER MOLE CO
1.0000   0.2083   0.7520  0.7113   0.7538   0.3324   1.2898   1.0980
           MOLE  PRODUCT PER MOLE ETHENE
2.9251   0.6093   2.1998  2.0806   2.2051   0.9725   3.7730   3.2120
```

```
RUN NO =  80  SAMPLE NO =  4

PRD NO   MOL PERCENT    MOLS/MOL N2    MOLS/MOXY R    MOLS/MBUT R
   1       0.490970       0.015562       0.061753       0.060507
   2       0.435583       0.013807       0.054786       0.053681
   3      31.547794       1.000000       3.968007       3.887963
   4       3.477710       0.110236       0.437418       0.428594
   5       0.874992       0.027735       0.110054       0.107834
   6       1.119781       0.035494       0.140843       0.138002
   7       0.258821       0.008204       0.032553       0.031897
   8       0.000000       0.000000       0.000000       0.000000
   9       1.658715       0.052577       0.208629       0.204420
  10       0.092682       0.002937       0.011657       0.011422
  11       0.585884       0.018571       0.073691       0.072204
  12       1.906960       0.060446       0.239852       0.235014
  13      48.881919       1.549456       6.148253       6.024228
  14       0.009952       0.000315       0.001251       0.001226
  15       0.011428       0.000362       0.001437       0.001408
  16       0.516662       0.016377       0.064984       0.063673
  17       3.774159       0.119633       0.474704       0.465129
  18       0.174567       0.005533       0.021956       0.021513
  19       2.310658       0.073243       0.290629       0.284766
  20       0.755790       0.023956       0.095061       0.093143
  21       0.000000       0.000000       0.000000       0.000000
  22       0.529407       0.016781       0.066587       0.065244
  23       0.049999       0.001584       0.006288       0.006161
  24       0.145623       0.004615       0.018316       0.017946
  25       0.074374       0.002357       0.009354       0.009165
  26       0.005476       0.000173       0.000688       0.000674
  27       0.018285       0.000579       0.002299       0.002253
  28       0.060940       0.001931       0.007664       0.007510
  29       0.231019       0.007322       0.029057       0.028470
  30       0.000000       0.000000       0.000000       0.000000

TOTALS    99.999938     100.000030       3.169794

CARBON   BALANCE      7.155912 LB AT/MOLN2.     99.02 PERCENT
HYDROGEN BALANCE     17.670410 LB AT/MOLN2.     97.80 PERCENT
OXYGEN BALANCE        0.428318 LB AT/MOLN2.     80.56 PERCENT

PERCENT O2 REACT     94.8059     PERCENT C4 REACT     14.2364

   CO        CO2    BUTEN    PARFIN   ALCOHL   ALDHYD   OXYGCO    WATER
            MOLE  PRODUCT  PER MOLE  N-BUTANE
0.4285    0.0636   0.3072   0.2002   0.3139   0.1348   0.5368   0.4651
            MOLE  PRODUCT  PER MOLE  N-BUTENES
1.3950    0.2072   1.0000   0.6517   1.0217   0.4389   1.7474   1.5139
            MOLE  PRODUCT  PER MOLE  CO
1.0000    0.1485   0.7168   0.4671   0.7324   0.3146   1.2525   1.0852
            MOLE  PRODUCT  PER MOLE  ETHENE
3.1057    0.4613   2.2261   1.4509   2.2746   0.9772   3.8901   3.3704
```

APPENDIX F

TRANSPORTED BED REACTOR MODEL

Derivation of the Rate Equations

The following reaction scheme was used for the preliminary evaluation of the TBR.

$$RH + O_2 \rightarrow \dot{R} + \dot{M} \tag{F.1}$$

$$\dot{R} + O_2 \rightarrow P + \dot{M} \tag{F.2}$$

$$P + O_2 \rightarrow Q + \dot{M} \tag{F.3}$$

$$RH + \dot{M} \rightarrow \dot{R} + S \tag{F.4}$$

$$\dot{M} \rightarrow \text{termination} \tag{F.5}$$

where RH stands for the hydrocarbon, $\dot{M}$ for free radical, $\dot{R}$ for alkyl radical, P for an intermediate and Q and S for end products.

Solution of these equations, using the method of quasi-stationary state in chain reaction mechanism leads to

$$\begin{aligned} C_{A_o}\frac{dx_A}{dt} = {} & K_1 C_{A_o} C_{B_o} (1 - x_A)(1 - x_B)\{1 + 2C_{A_o} K_3 (1 - x_A)\} \\ & + C_{A_o}^{\ 2}\, C_{B_o}\, K_2 K_3 (1 - x_A)(1 - x_B) x_C \end{aligned} \tag{F.6}$$

$$= K_1 C_1 (1 + 2K_3 C_7) + K_2 K_3 C_{A_o} C_1 x_C \tag{F.7}$$

where $C_1 = C_{A_o} C_{B_o} (1 - x_A)(1 - x_B)$

$C_2 = C_{A_o} C_{B_o} (1 - x_B) x_C$

$C_7 = C_{A_o} (1 - x_A)$ and

C_{A_o} and C_{B_o} are the initial concentrations of <u>n</u>-butane and oxygen, respectively, x_A and x_B their conversions, and x_C the accumulation of the intermediate species P expressed as

$$x_C = \frac{C_c}{C_{A_o}}$$

where C_c is the concentration of the species P.

The rate constant K_3 above is in fact the ratio of rate constants for reactions (4) and (5).

The other two rate equations are:

$$C_{B_o}\frac{dx_B}{dt} = (2K_1C_1 + K_2C_2)(1 + K_3C_{A_o}C_7) \qquad \text{(F.8)}$$

$$C_{A_o}\frac{dx_C}{dt} = K_1C_1(1 + 2K_3C_7) + K_2C_2(K_3C_7C_{A_o} - 1) \qquad \text{(F.9)}$$

An overall heat of reaction is used and is combined with the conversion equation for oxygen as the heat generation term in equation 7.3.

Derivation of the Heat Conduction Equation

Assumptions:

1. Solids temperature symmetrical.
2. Thermal conductivity and specific heat of solids are constant.
3. Neglect all second order or higher differentials (dr).

Consider as in figure F.1 a heat balance about a spherical shell of radius r and thickness dr.

Heat in $= -\,4\pi r^2 K_s(\frac{\partial v}{\partial r})dt$

Heat out $= -\,4\pi(r + dr)^2 K_s(\frac{\partial v}{\partial r} + \frac{\partial}{\partial r}\frac{\partial v}{\partial r}\,dr)dt$

Accumulation $= \rho_s c_s\,\frac{4}{3}\pi\,[(r + dr)^3 - r^3]\,dv$

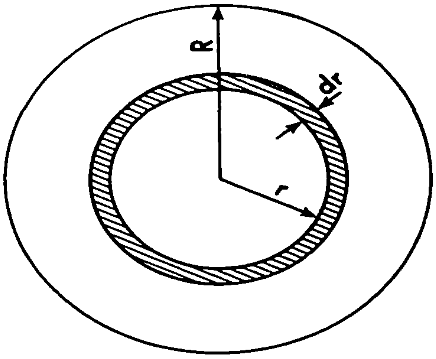

FIGURE F.1 HEAT BALANCE FOR A SPHERICAL PARTICLE

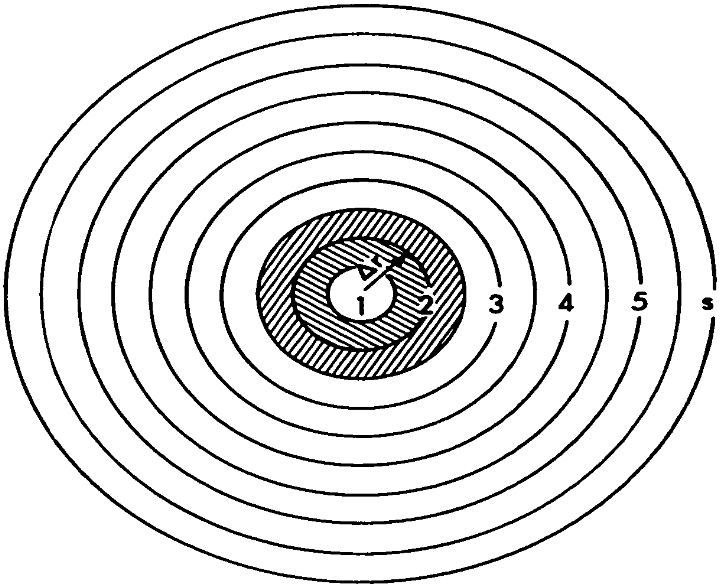

FIGURE F.2 DISCRETISATION OF THE SPHERICAL SHELL

$$\therefore\ 4\pi(r + dr)^2 K_s\left(\frac{\partial v}{\partial r} + \frac{\partial}{\partial r}\frac{\partial v}{\partial r}\,dr\right)dt - 4\pi r^2 K_s\left(\frac{\partial v}{\partial r}\right)dt$$

$$= \rho_s C_s \frac{4}{3}\pi[(r + dr)^3 - r^3]dv$$

Multiplying and neglecting all terms $(dr)^2$ and higher

$$4\pi r^2 K_s \frac{\partial^2 v}{\partial r^2} dr + 8\pi r dr K_2 \frac{\partial v}{\partial r} = \frac{4}{3}\pi\rho_s C_s(r^3 + 3r^3 dr - r^3)\frac{\partial v}{\partial t}$$

$$\therefore\ 4\pi r^2 K_s dr \frac{\partial^2 v}{\partial r^2} + 8\pi r\, dr K_2 \frac{\partial v}{\partial r} = 4\pi^2 dr \rho_s C_s \frac{\partial v}{\partial t}$$

$$\therefore\ \frac{K_s}{\rho_s C_s}\left(\frac{\partial^2 v}{\partial r^2} + \frac{2}{r}\frac{\partial v}{\partial r}\right) = \frac{\partial v}{\partial t}$$

But $\frac{K_s}{\rho_s C_s} = \alpha$, the thermal diffusivity

$$\therefore\ \frac{\partial v}{\partial t} = \alpha\left(\frac{\partial^2 v}{\partial r^2} + \frac{2}{r}\frac{\partial v}{\partial r}\right) \qquad \text{(F.10)}$$

$$\text{or,}\ \frac{\partial v}{\partial t} = \frac{\alpha}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial v}{\partial r}\right) \qquad \text{(F.11)}$$

Using the property

$$\frac{\partial f}{\partial \eta} = \frac{\partial f}{\partial \xi}\frac{d\xi}{d\eta}\ \text{, where } \xi \text{ is a function of } \eta \text{ only,}$$

in the above equation $f = r^2 \frac{\partial v}{\partial r}$, $\xi = r^3$ and $\eta = r$, equation (F.11) reduces to the form

$$\frac{\partial v}{\partial t} = 3\alpha \frac{\partial}{\partial r^3}\left(r^2\frac{\partial v}{\partial r}\right) \qquad \text{(F.12)}$$

This equation is reduced to a convenient form by descretizing the space derivative while treating the time derivative as a continuous derivative.

Discretisation of the Heat Conduction Equation

For a sphere divided into five equal segments as in figure (F.2), the discretisation of the space variable in equation (F.12) gives, for point 1,

$$\frac{dv_1}{dt} = 3\alpha[\frac{(\frac{r_2 + r_1}{2})^2(\frac{v_2 - v_1}{r_2 - r_1})}{(\frac{r_2 + r_1}{2})^3}$$

$$= 3\alpha\,\frac{\Delta r}{4}\,\frac{-v_1 + v_2}{\frac{\Delta r^3}{8}}$$

$$= \frac{6\alpha}{\Delta r^2}\,(-\,v_1 + v_2)$$

$$\text{or, }\quad \frac{1}{6}\,\frac{dv_1}{dt} = \frac{\alpha}{\Delta r^2}(-\,v_1 + v_2) \tag{F.13}$$

For point 2,

$$\frac{dv_2}{dt} = 3\alpha\,\frac{(\frac{r_3 + r_2}{2})^2\,(\frac{v_3 - v_2}{r_3 - r_2}) - (\frac{r_2 + r_1}{2})^2\,(\frac{v_2 - v_1}{r_2 - r_1})}{(\frac{r_2 + r_3}{2})^3 - (\frac{r_2 + r_1}{2})^3}$$

$$= 3\alpha\,\frac{\Delta r}{4}\,\frac{9(v_3 - v_2) - (v_2 - v_1)}{\Delta r^3\,(\frac{27}{8} - \frac{1}{8})}$$

$$= \frac{3}{13}\,\frac{\alpha}{\Delta r^2}\,(v_1 - 10v_2 + 9v_3)$$

$$\text{or, }\quad \frac{13}{3}\,\frac{dv_2}{dt} = \frac{\alpha}{\Delta r^2}\,(v_1 - 10v_2 + 9v_3) \tag{F.14}$$

For point 3,

$$\frac{dv_3}{dt} = 3\alpha\,\frac{(\frac{r_4 + r_3}{2})^2\,(\frac{v_4 - v_3}{r_4 - r_3}) - (\frac{r_3 + r_2}{2})^2\,(\frac{v_3 - v_2}{r_3 - r_2})}{(\frac{r_4 + r_3}{2})^3 - (\frac{r_3 + r_2}{2})^3}$$

or, $\frac{49}{3}\frac{dv_3}{dt} = \frac{\alpha}{\Delta r^2}\,(9v_2 - 34v_3 + 25v_4)$ (F.15)

For point 4,

$$\frac{dv_4}{dt} = 3\alpha\,\frac{(\frac{r_5 + r_4}{2})^2\,(\frac{v_5 - v_4}{r_5 - r_4}) - (\frac{r_4 + r_3}{2})^2\,(\frac{v_4 - v_3}{r_4 - r_3})}{(\frac{r_5 + r_4}{2})^3 - (\frac{r_4 + r_3}{2})^3}$$

or, $\frac{109}{3}\frac{dv_4}{dt} = \frac{\alpha}{\Delta r^2}\,(25v_3 - 74v_4 + 49v_5)$ (F.16)

For point 5,

$$\frac{dv_5}{dt} = 3\alpha\,\frac{(\frac{r_5 + \Delta r + r_5}{2})^2(\frac{v_5 - v_5}{r_5 + \Delta r - r_5}) - (\frac{r_5 + r_4}{2})^2(\frac{v_5 - v_4}{r_5 - r_4})}{(\frac{r_5 + \Delta r + r_5}{2})^3 - (\frac{r_5 + r_4}{2})^3}$$

or, $\frac{193}{3}\frac{dv_5}{dt} = \frac{\alpha}{\Delta r^2}\,(49v_4 - 130v_5 + 81v_5)$ (F.17)

Equations (F.4) to (F.8) are now in the form

$$\underline{G}\,\frac{d\underline{v}}{dt} = \frac{\alpha}{\Delta r^2}\,(\underline{B}\;\underline{v} + \underline{S}'(t)) \qquad \text{(F.18)}$$

where

$$\underset{=}{G} = \begin{bmatrix} 1/6 & 0 & 0 & 0 & 0 \\ 0 & 13/3 & 0 & 0 & 0 \\ 0 & 0 & 49/3 & 0 & 0 \\ 0 & 0 & 0 & 109/3 & 0 \\ 0 & 0 & 0 & 0 & 193/3 \end{bmatrix} \qquad (F.19)$$

$$\underset{=}{B} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ 1 & -10 & 9 & 0 & 0 \\ 0 & 9 & -34 & 25 & 0 \\ 0 & 0 & 25 & -74 & 49 \\ 0 & 0 & 0 & 49 & -130 \end{bmatrix} \qquad (F.20)$$

and

$$S'(t) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 81v_s \end{bmatrix} \qquad (F.21)$$

In order to make the solution independent of the properties of the solids and the diameter of the solid particles, the equation (F.18) is nondimensionalized.

Let

$$\theta = \frac{\alpha t}{\Delta r^2}$$

$$d\theta = \frac{\alpha}{\Delta r^2}\, dt$$

$$\therefore\ \underline{G}\, \frac{d\underline{v}}{d\theta}\, \frac{\alpha}{\Delta r^2} = \frac{\alpha}{\Delta r^2}\, [\underline{B}\ \underline{v} + \underline{S}(\theta)]$$

$$\underline{G}\, \frac{d\underline{v}}{d\theta} = \underline{B}\ \underline{v} + \underline{S}(\theta) \qquad (F.22)$$

<u>Method of Solution</u>

The solution to this matrix differential equation has been obtained in a closed form as:

$$\underline{v}(\theta,r) = \underline{G}^{-1/2}\underline{Q}\ \underline{E}(\theta)\underline{Q}^T\underline{G}^{1/2}[\underline{v}^{(0)} + \int_0^\theta \underline{G}^{-1/2}\underline{Q}\ \underline{E}^{-1}(\sigma)\underline{Q}^T\underline{G}^{-1/2}\, \underline{S}(\sigma)\, d\sigma] \qquad (F.23)$$

A direct numerical solution to this leads to instability. A numerically suitable form can be obtained by simplification of the above. Multiplying out the terms, one obtains

$$\underline{v}(\theta,r) = \underline{G}^{-1/2}\underline{Q}\ \underline{E}(\theta)\underline{Q}^T\underline{G}^{1/2}\underline{v}^{(0)} + \underline{G}^{-1/2}\underline{Q}\ \underline{E}(\theta)\int \underline{E}^{-1}(\sigma)\underline{Q}^T\underline{G}^{-1/2}\underline{S}(\sigma)d\sigma$$

$$= \underline{G}^{-1/2}\underline{Q}[\underline{E}(\theta)\underline{Q}^T\underline{G}^{1/2}\underline{v}^{(0)} + \underline{E}(\theta)\int_0^\theta \underline{E}^{-1}(\sigma)\underline{Q}^T\underline{G}^{-1/2}\underline{S}(\sigma)d\sigma]$$

$$= \underline{D}[\underline{E}(\theta)\ \underline{V}\ \underline{v}^{(0)} + \underline{E}(\theta)\int_0^\theta \underline{E}^{-1}(\sigma)\ \underline{H}\ \underline{S}(\sigma)\ d\sigma\ ] \qquad (F.24)$$

where $\underline{D} = \underline{G}^{-1/2}\,\underline{Q}$, $\underline{V} = \underline{Q}^T\underline{G}^{1/2}$ and $\underline{H} = \underline{Q}^T\underline{G}^{-1/2}$.

If the boundary condition vector is of the form

$$\underline{S}(\theta) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \phi(\theta) \end{bmatrix} ,$$

the matrix $\underline{H}$ can be replaced by a vector $\underline{p}$, which is the last column for the matrix $\underline{H}$. The second term in equation (F.15) is thus

$$\underline{E}(\theta) \int_0^\theta E^{-1}(\sigma)\underline{p}\ \phi(\sigma)\, d\sigma \tag{F.25}$$

Realizing that the matrices $E(\theta)$ and $E^{-1}(\sigma)$ are diagonal matrices, the above integration and the subsequent multiplication can be performed term by term. Considering the ith element, the above term is,

$$e^{\lambda_i\theta} \int_0^\theta e^{-\lambda_i\sigma}\ p_i\ \phi(\sigma)\, d\sigma \tag{F.26}$$

The integral can be evaluated for any function $\phi(\sigma)$. If

$$\phi(\sigma) = a_o + b\sigma \quad , \tag{F.27}$$

Integration by parts leads to

$$e^{\lambda_i\theta}\,[(\frac{a_o}{\lambda_i} + \frac{b}{\lambda_i^2})(1 - e^{-\lambda_i\theta}) - \frac{b}{\lambda_i}\,\theta\, e^{-\lambda_i\theta}]v_i$$

$$= v_i[(\frac{a_o}{\lambda_i} + \frac{b}{\lambda_i^2})\,(e^{\lambda_i\theta} - 1) - \frac{b}{\lambda_i}\,\theta] \qquad (F.28)$$

The first term in the parenthesis in equation (F.24) is obtained by post multiplying the matrix $\underline{V}$ with the initial condition vector $\underline{v}^{(0)}$ and premultiplying the resultant vector with the matrix $\underline{E}(\theta)$.

The two parts of the solution are then combined and multiplied by matrix $\underline{D}$ to obtain the temperatures.

The heat transfer from the gas to the solids is given by

$$Q_g = [(cT_2 + cT_1)G_g - h_w A_w(T - T_w)dZ + A_r dZ(-r\Delta H)]\theta \qquad (F.29)$$

This must be equal to the heat received by the solids:

$$Q_s = h_c A_s dZ(T - v_s)\theta = A_s dZ \int_0^\theta K_s(\frac{\partial v}{\partial r})_{r=R}\, d\theta \qquad (F.30)$$

This can be more easily obtained by integrating over the whole surface of the solids.

$$Q_s = NdZ \int_0^R C_p \rho_p\; 4\pi r^2(\underline{v}^{(1)} - \underline{v}^{(0)})dr \quad , \qquad (F.31)$$

where $\underline{v}^{(0)}$ and $\underline{v}^{(1)}$ are the temperatures at the beginning and at the end of the increments respectively.

The algorithm is now as follows:

1. Assume $a_o = v_s^{(0)}$, where $v_s^{(0)}$ is the initial condition or is known from the previous increment. Obtain $v_s^{(1)}$ by a heat balance at the

surface.

2. Obtain $b = \dfrac{v_s^{(1)} - a_o}{\theta}$
3. Solve the gas phase equations.
4. Obtain Q_g.
5. Solve the matrix differential equation for the solids phase.
6. Obtain Q_s.
7. If $|Q_g - Q_s| < \varepsilon$, go to next increment and repeat.
8. If $|Q_g - Q_s| > \varepsilon$, obtain a new b as follows:

$$Q = h_c A_s dZ(T - v_s), \text{ where}$$

$$Q = \frac{Q_s + Q_g}{2} \text{ and } v_s = a_o + \frac{1}{2} b\theta$$

$$\therefore \quad b = \frac{2}{\theta} \left(T - a_o - \frac{Q}{h_c A_s dZ\theta}\right)$$

Perturb b if necessary.

9. Go to 3 and interate.

A value of 0.05 has been used in the calculations for λ which has been redefined as

$$\lambda = \frac{2|Q_g - Q_s|}{|Q_g + Q_s|}$$

The value of the perturbation factor for b depends on the diameter of the particle and is obtained by trial and error.

The computer program and some sample results are now presented.

```
      C        TBR

C       TBR

C       THIS PROGRAM SOLVES A COUPLED SYSTEM OF A SET OF
C       ORDINARY DIFFERENTIAL EQUATIONS AND A PARABOLIC
C       PARTIAL DIFFERENTIAL EQUATION. THE SYSTEM IS DECOU-
C       PLED AND SOLVED SEPARATELY.
C       THE STATE VARIABLES ARE NORMALISED SO THAT THEIR
C       VALUES DO NOT EXCEED 12.0.
C       THE PERTURBATION FACTOR IS OBTAINED BY TRIAL AND
C       ERROR, USUALLY STARTING AT A LOWER VALUE AND
C       SLOWLY INCREASING TO THE DESIRED VALUE.
C       THE PROGRAM USES NINE SUBROUTINES INCLUDING THE
C       FORS SUBROUTINE FOR WALL TEMPERATURE PROFILE.
C       THE SUBROUTINES ARE PRESENTED FOLLOWED BY THE
C       MAINLINE PROGRAM. THE PURPOSE OF EACH SUBROUTINE
C       IS OUTLINED AT THE BEGINNING OF EACH SUBROUTINE.
C       THE MAINLINE PROGRAM READS IN THE INITIAL CONDI-
C       TIONS AND INPUT MATRICES, DIRECTS THE SOLUTION
C       AND PRINTS OUT THE RESULTS.
C

      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION TY(8),D(8),QR(8),AA(8),EA(8),TT(12),R(12)
     *,W(8)
      DIMENSION T(200,12),S(8,4),U(12)
      DIMENSION A(78),UO(12),TC2(12),TN(12)
      DIMENSION B(12,12),V(12,12),G(12,12),TI(8)

C         M    NUMBER OF REACTION EQUATIONS 9
C         N    NUMBER OF RADIAL DIVISIONS 13
C         MM   NUMBER OF DIFFERENTIAL EQUATIONS 9
C         MG   NUMBER OF GAS FLOW RATES
C         ML   NUMBER OF LOADING RATIOS
C         MR   NUMBER OF PARTICLE DIAMETERS
C         MT   NUMBER OF PARTICLE MATERIALS
C         N4   NUMBER OF INCREMENTS ALONG LENGTH OF REACTOR
C         DIF TEMPERATURE DIFFERENCE BETWEEN GAS AND SOLIDS
C         SURFACE
C         DL LENGTH ALONG REACTOR
C         ES   ALLOWABLE ERROR IN BOUNDARY CONDITION MATCHING
C         FL   LENGTH OF REACTOR
C         FT   PERTURBATION FACTOR FOR MATCHING
C         HR   HEAT OF REACTION
C         T    TEMPERATURE OF SOLID PARTICLES
C         TB   BASE TEMPERATURE
C         TG   TEMPERATURE OF GAS
C         TS   SURFACE TEMPERATURE OF PARTICLES
C         TW   WALL TEMPERATURE OF REACTOR
C         XA   CONVERSION OF BUTANE
```

```
         C         TBR               ...(CONT'D)
C         XB  CONVERSION OF OXYGEN
C         XC  ACCUMMULATION OF INTERMEDIATE
C
    1 FORMAT(5F15.0)
    2 FORMAT(7F10.0)
    3 FORMAT(17X,7F10.4)
    4 FORMAT(7I4)
    5 FORMAT(3F10.0)
    6 FORMAT(20X,7F10.3)
    7 FORMAT(31X,3F15.5)
    8 FORMAT(19X,3F10.5,2F9.3,F12.4,F8.3)
    9 FORMAT(18X,5F15.5)
   10 FORMAT(18X,10I10)
  432 FORMAT(10X,28HENERGY BALANCE DID NOT MATCH)
  433 FORMAT(//45X,24HINITIAL CONDITION VECTOR/)
  434 FORMAT(//45X,25HBOUNDARY CONDITION VECTOR/)
  435 FORMAT(//50X,8HMATRIX G/)
  436 FORMAT(//50X,8HMATRIX B/)
  437 FORMAT(//47X,18HKINETIC PARAMETERS/)
  438 FORMAT(//20X,41HINITIAL CONDITION FOR GAS PHASE
     * EQUATIONS/)
  491 FORMAT(1H1)
  492 FORMAT(//20X,20HPARTICLE DIAMETER = ,F6.2,3X
     *,16HLOADING RATIO = ,F
     24.1,3X,17HSCALING FACTOR = ,F6.1)
  493 FORMAT(//22X,2HXA,9X,2HXB,9X,2HXC,9X,2HVG,7X,2HVP,6X
     *,2HTG,7X,2HDL)
  494 FORMAT(/20X,4HT(1),7X,4HT(2),6X,4HT(3),6X,4HT(4),6X
     *,4HT(5),6X,2HTS
     2,9X,3HDIF/)
  495 FORMAT(1X,////)
  499 FORMAT(28X,20HPARTICLE DIAMETER = ,F6.2,3X,16HLOADING
     * RATIO = ,F4.
     21)
  531 FORMAT(20X,7F10.4)
  710 FORMAT(7F10.0)
  711 FORMAT(//20X,19HGAS PHASE CONSTANTS//18X,5F15.5)
  712 FORMAT(//20X,29HPROPERTIES OF SOLID PARTICLES//18X
     *,5F15.5)
  714 FORMAT(//20X,44HPOLYNOMIAL COEFFICIENTS FOR WALL
     * TEMPERATURE//18X,
     25F15.5)
  805 FORMAT(10X,4E18.5)
      WRITE(6,495)


      READ(5,4)N3,N4,M,N,MM,MP,ML
      WRITE(6,10)N3,N4,M,N,MM,MP,ML
      READ(5,4)MG,MT,MR,NGT,NPT,KQT
```

```
C         TBR                  ...(CONT'D)
      WRITE(6,10)MG,MT,MR,NGT,NPT,KQT
C        READ IN CONSTANTS
C
      READ(5,2)PR,RR,GC,FR,FL,DRR,ZO
      WRITE(6,6)PR,RR,GC,FR,FL,DRR,ZO
      READ(5,2)TB,HR,FIF,ES,C,TO
      WRITE(6,6)TB,HR,FIF,ES,C,TO
C        READ IN REACTION PARAMETERS
C
      READ(5,5)(EA(I),AA(I),W(I),I=1,M)
      WRITE(6,437)
      WRITE(6,7)(EA(I),AA(I),W(I),I=1,M)
C        READ IN INITIAL CONDITION FOR GAS PHASE EQUATIONS
C
      READ(5,2)(TI(I),I=1,MM)
C        READ IN MATRICES AND VECTORS FOR SOLIDS PDE
C
      READ(5,1)((G(I,J),J=1,N),I=1,N)
      WRITE(6,435)
      WRITE(6,9)((G(I,J),J=1,N),I=1,N)
      READ(5,1)((B(I,J),J=1,N),I=1,N)
      WRITE(6,436)
      WRITE(6,9)((B(I,J),J=1,N),I=1,N)
      READ(5,1)(UO(I),I=1,N)
      WRITE(6,433)
      WRITE(6,9)(UO(I),I=1,N)
      READ(5,1)(U(I),I=1,N)
      WRITE(6,434)
      WRITE(6,9)(U(I),I=1,4)
      WRITE(6,491)
      WRITE(6,495)
C        DO THE MATRIX CALCULATIONS
C        FIND EIGENVALUES AND EIGENVECTORS
C
      CALL CLMT(G,B,V,A,N)
      GD=GC*RR
      HR=HR*1000.0
      FN3=N3
      FN4=N4
      DRR=DRR/12.0
```

```
      C          TBR                ...(CONT'D)

      ARR=0.785*DRR**2
      AW=3.1417*DRR
      DZ=FL/FN4
C        START THE CALCULATIONS
C

      DO 600 LG=1,MG
C        READ IN THE CONSTANTS FOR GAS PHASE
C

      READ (5,710)WQ,WM,TGO,TO
      WRITE(6,711)WQ,WM,TGO,TO
      RR=RR/WM
C        READ IN PROPERTIES OF MATERIALS OF THE SOLID
C        PARTICLES
C

      DO 600 LT=1,MT
      READ(5,710)DS,CS,SK
      WRITE(6,712)DS,CS,SK
      AL=SK/(DS*CS)
C        READ IN THE PARTICLE DIAMETER,INITIAL PARTICLE
C        PARTICLE
C        VELOCITY AND THE PERTURBATION FACTOR
C

      DO 600 LR=1,MR
      READ(5,710) RA,VPO,FT
      DP=2.0*RA
C        READ IN THE LOADING RATIO
C

      DO 600 LK=1,ML
      READ(5,710)SOG
      WP=SOG*WQ
C        READ IN THE POLYNOMIAL COEFFICIENTS FOR WALL
C        TEMPERATURE
C

      READ (5,710)A1,A2,A3,A4
      WRITE(6,714)A1,A2,A3,A4


      WRITE(6,492)DP,SOG,FT
```

```
C          TBR                  ...(CONT'D)
      FTO=FT
      GM=WQ/WM
      WG=WQ/ARR
      GS=WG/WM
      B3=0.05*GM*HR
      RA=RA*3.28E-06
      DR=RA/FN3
      DO 13 I=1,N
      FI=I-1
   13 R(I)=FI*DR
      DO 14 I=1,N
      TN(I)=TO-460.0
      TT(I)=TO
   14 CONTINUE
      DST=TO
      XO=0.0
      IA=1
      DO 18 I=1,N
   18 T(IA,I)=TO
      DG=(WM*PR)/(10.73*TGO)
      VG=WG/DG
      VG=VG/3600.0
      TI(7)=VG
      WRITE(6,438)
      WRITE(6,531)(TI(I),I=1,MM)
      WRITE(6,491)
      WRITE(6,495)
      WRITE(6,499) DP,SOG
      DP=DP*3.28E-06
      TI(4)=TGO/TB
      TI(6)=VPO
      TI(5)=TO/TB
      DO 31 I=1,MM
      TY(I)=TI(I)
   31 CONTINUE
      WS=WP/ARR
      CK=3.0*WP*CS*DZ
      CAO=0.20*DG/WM
      CBO=0.05*DG/WM
      VP=TY(6)
      TG=TY(4)*TB
      TP=TY(5)*TB
      DSTP=DST-460.0
      TGP=TGO-460.0
      DF=TGP-DSTP
      LP=0
      WRITE(6,493)
      WRITE(6,494)
      WRITE(6,8)TI(1),TI(2),TI(3),TI(7),TI(6),TGP,XO
      WRITE(6,3)(TN(I),I=1,N),DSTP,DF
```

```
          C        TBR

C        TBR
  503 DG=(WM*PR)/(10.73*TG)
      CPG=0.1903+1.8E-04*TG-3.147E-08*TG**2
      UG=0.04598+0.00004556*(TG-660.0)
      TKG=0.01762+0.0000233*(TG-660.0)
      HW=0.16*TKG/DRR*(WS/WG)**0.45*(DRR*WG/UG)**0.6*(CPG*UG
     */TKG)**0.4
      HC=0.16*(TKG/DP)*(DP*WG/UG)**0.5
      UG=UG/3600.0
      VT=(2.4*(DS-DG)**0.673*DP**1.02)/(DG**0.327*UG**0.347)
      STG=SOG*VG/VP
      E=STG*DG/DS
      E=1.0-E

C        CONSTANTS FOR ENERGY EQUATIONS
C

      F1=(4.0*HW)/(DRR*CPG*WG)
      F3=(0.05*HR)/(CPG*WM)
      F6=E/(0.05*GS)
      F3=F3/TB
      B1=HW*AW
      B4=12.0*DR*HC/SK
      B2=DG/WG

C        CONSTANTS FOR MOMENTUM EQUATIONS
C

      UGU=ABS(VG-VP)
      RNP=DP*DG*UGU/UG
      RNP=SQRT(RNP)
      CD=0.64+4.8/RNP
      CD=CD**2
      FF1=0.75*CD*DG*UGU/(DP*DS)
      C8=VP*RA*RA*3600.0*RA
      CP=CK/C8
      DT=DZ/(VP*3600.0)
      DTM=AL*DT/DR
      DTM=DTM/DR
      DC=DTM
      AS=6.0*WP/(VP*DP*DS*3600.0)
      F2=STG*CS/CPG
      F4=VP*DS*CS*DP*3600.0
      F5=6.0*HC/F4
      F7=HC*AS*DZ*DT
  103 P=T(IA,N)
      TS=B4*TG+18.0*T(IA,N-1)-9.0*T(IA,N-2)+2.0*T(IA,N-3)
      TS=TS/(11.0+B4)
      C5=TG*CPG*WM
      KQ=0
```

```
C        TBR                 ...(CONT'D)

      F=(TS-P)/DTM
      IN=0
      IP=0
  100 KQ=KQ+1
      IF(IN-NGT)105,105,65
  105 IF(IP-NPT)102,102,65
C
C         SOLVE THE GAS PHASE DIFFERENTIAL EQUATIONS
C
  102 CALL GENER(TY,D,W,AA,EA,XO,DZ,MM,M,P,F,DC,STG,TW)
C
C         OBTAIN THE ENTHALPY BALANCE FOR THE GAS PHASE
C
      C4=D(4)*TB*CPG*WM
      Q2=((C5-C4)*GM-B1*DZ*(D(4)-TW)*TB+B3*(D(2)-TY(2)))*DT
C
C         CALL THE SUBROUTINES FOR CALCULATION OF SOLIDS
C         TEMPERATURES
C         AND SOLIDS ENTHALPY BALANCE
C
      CALL SIMPS(N,F,P,DTM,A,TC2,G)
      CALL TMDEF(B,V,G,T,TT,Q1,R,TS,DR,CP,DTM,IA,N,A,TC2)
      IF(Q1)407,408,408
C
C         MATCH THE SOLIDS AND GAS ENTHALPT BALANCES
C
  408 TES= ABS(Q1-Q2)
      AQ= ABS(Q1+Q2)
      TES=TES*2.0/AQ
      IF(TES-ES)50,50,412
  412 Q3=(Q1+Q2)/2.0
      Q5=F7*(D(4)*TB-P-F*0.5*DTM)
      QC=Q3/F7
      F=(D(4)*TB-P-QC)/(0.5*DTM)
      IF(KQ-KQT)410,410,407
C
C         PERTURB THE MATCHING FACTOR
C
  410 F=F/FT
      GO TO 100
C
C         SEARCH FOR THE MATCHING FACTOR
C
  407 FT=FT+0.01*FT
```

```
      C          TBR               ...(CONT'D)
      F=F/FT
      IN=IN+1
      KQ=0
      GO TO 100
C
C         MATCHING HAS BEEN OBTAINED
C
   50 TY(1)=D(1)
      TY(2)=D(2)
      TY(3)=D(3)
      TY(4)=D(4)
      TY(5)=D(5)
      TY(6)=D(6)
      TY(7)=D(7)
      XO=XO+DZ
      TG=TY(4)*TB
      TP=TY(5)*TB
      DST=F*DTM+P
      IA=IA+1
      DO 46 I=1,N
   46 T(IA,I)=TT(I)
      DO 77 I=1,N
      TN(I)=TT(I)-460.0
   77 CONTINUE
      TGP=TG-460.0
      DSTP=DST-460.0
      DF=TG-DST
      VP=TY(6)
      VG=TY(7)
      TWB=TW*TB-460.0
      IF(DF.LT.20.0) GO TO 579
      LN=-1
      GO TO 581
  579 LN=0
  581 IF(IA.GT.N4) GO TO 66
      LP=LP+1
      IF(LP.EQ.10) GO TO 507
      GO TO 509
  507 WRITE(6,8)TY(1),TY(2),TY(3),VG,VP,TGP,XO
      WRITE(6,3)(TN(I),I=1,N),DSTP,DF
      LP=0
  509 IF(LN.EQ.0) GO TO 517
      ES=0.05
      GO TO 503
  517 ES=0.10
      GO TO 503
   65 WRITE(6,8)TY(1),TY(2),TY(3),VG,VP,TGP,XO
      WRITE(6,3)(TN(I),I=1,N),DSTP,DF
      WRITE(6,491)
```

```
      C            TBR                     ...(CONT'D)

      WRITE(6,432)
   66 GO TO 600
  600 CONTINUE
      CALL EXIT
      END
```

SUBROUTINE CLMT

```
      SUBROUTINE CLMT(G,B,V,A,N)
C
C        THIS SUBROUTINE CALCULATES THE CONSTANTS IN THE
C        SOLUTION
C        OF THE MATRIX DIFFERENTIAL EQUATION.
C

      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION G(12,12),B(12,12),V(12,12),GG(12,12),G1(12
     *,12)
      DIMENSION QT(12,12),QP(12,12),A(78),Q(78),AR(12)

    9 FORMAT(18X,5F15.6)
   41 FORMAT(//50X,8HMATRIX K/)
   42 FORMAT(//50X,11HEIGENVALUES/)
   43 FORMAT(//50X,12HEIGENVECTORS/)

      DO 10 I=1,N
      DO 10 J=1,N
      IF(I-J)11,12,11
   11 GG(I,J)=0.0
      G1(I,J)=0.0
      G(I,J)=0.0
      GO TO 10
   12 G(I,I)=G(I,I)
      GG(I,I)=1.0/(SQRT(G(I,I)))
      G1(I,I)=SQRT(G(I,I))
   10 CONTINUE
C
C        CALCULATE MATRIX K
C
      CALL GMPRD(GG,B,V,N,N,N)
      CALL GMPRD(V,GG,B,N,N,N)
      WRITE(6,41)
      WRITE(6,9)((B(I,J),J=1,N),I=1,N)
C
C        CONVERT MATRIX K TO STORAGE MODE 1
C
      JJ=1
      DO 21 J=1,N
      DO 21 I=1,J
      A(JJ)=B(I,J)
      JJ=JJ+1
   21 CONTINUE
```

SUBROUTINE CLMT ...(CONT'D)

```
C     FIND EIGENVALUES OF MATRIX K
C
      MV=0
      CALL EIGEN(A,Q,N,MV)
C     SORT OUT EIGENVALUES
C
      JJ=1
      DO 22 I=1,N
      IF(I-1)15,15,16
   16 JJ=JJ+I
   15 A(I)=A(JJ)
      AR(I)=1.0/A(I)
   22 CONTINUE
      WRITE(6,42)
      WRITE(6,9)(A(I),I=1,N)
C     SORT OUT EIGENVECTORS
C
      DO 19 J=1,N
      DO 19 I=1,N
      JK=(J-1)*N+I
      QP(I,J)=Q(JK)
      QT(J,I)=QP(I,J)
   19 CONTINUE
      WRITE(6,43)
      WRITE(6,9)((QP(I,J),J=1,N),I=1,N)
      CALL GMPRD(GG,QP,B,N,N,N)
      CALL GMPRD(QT,G1,V,N,N,N)
      CALL GMPRD(QT,GG,G,N,N,N)
      RETURN
      END
```

SUBROUTINE EIGEN

```
      SUBROUTINE EIGEN(A,R,N,MV)
C          THIS SUBROUTINE CALCULATES THE EIGENVALUES AND
C          EIGENVECTORS
C          OF A SYMMETRIC MATRIX BY THE METHOD OF JACOBI. THIS
C          ROUTINE
C          IS REPRODUCED FROM IBM SCIENTIFIC SUBROUTINE
C          PACKAGE.
C
      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION A(78),R(78)
C          GENERATE IDENTITY MATRIX
C
C   5 RANGE=1.0D-12
    5 RANGE=1.0E-12
      IF(MV-1) 10,25,10
   10 IQ=-N
      DO 20 J=1,N
      IQ=IQ+N
      DO 20 I=1,N
      IJ=IQ+I
      R(IJ)=0.0
      IF(I-J) 20,15,20
   15 R(IJ)=1.0
   20 CONTINUE
C          COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)
C
   25 ANORM=0.0
      DO 35 I=1,N
      DO 35 J=I,N
      IF(I-J) 30,35,30
   30 IA=I+(J*J-J)/2
      ANORM=ANORM+A(IA)*A(IA)
   35 CONTINUE
      IF(ANORM) 165,165,40
C  40 ANORM=1.414*DSQRT(ANORM)
   40 ANORM=1.414* SQRT(ANORM)
      ANRMX=ANORM*RANGE/FLOAT(N)
C          INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
C
```

SUBROUTINE EIGEN ...(CONT'D)

```
      IND=0
      THR=ANORM
   45 THR=THR/FLOAT(N)
   50 L=1
   55 M=L+1
C
C         COMPUTE SIN AND COS
C
   60 MQ=(M*M-M)/2
      LQ=(L*L-L)/2
      LM=L+MQ
C
C  62 IF(DABS(A(LM))-THR) 130,65,65
C
   62 IF( ABS(A(LM))-THR) 130,65,65
   65 IND=1
      LL=L+LQ
      MM=M+MQ
      X=0.5*(A(LL)-A(MM))
   68 Y=-A(LM)/ SQRT(A(LM)*A(LM)+X*X)
      IF(X) 70,75,75
   70 Y=-Y
C
C  75 SINX=Y/DSQRT(2.0*(1.0+(DSQRT(1.0-Y*Y))))
C
   75 SINX=Y/ SQRT(2.0*(1.0+( SQRT(1.0-Y*Y))))
      SINX2=SINX*SINX
C
C  78 COSX=DSQRT(1.0-SINX2)
C
   78 COSX= SQRT(1.0-SINX2)
      COSX2=COSX*COSX
      SINCS =SINX*COSX
C
C         ROTATE L AND M COLUMNS
C
      ILQ=N*(L-1)
      IMQ=N*(M-1)
      DO 125 I=1,N
      IQ=(I*I-I)/2
      IF(I-L) 80,115,80
   80 IF(I-M) 85,115,90
   85 IM=I+MQ
      GO TO 95
   90 IM=M+IQ
   95 IF(I-L) 100,105,105
  100 IL=I+LQ
      GO TO 110
```

SUBROUTINE EIGEN ...(CONT'D)

```
  105 IL=L+IQ
  110 X=A(IL)*COSX-A(IM)*SINX
      A(IM)=A(IL)*SINX+A(IM)*COSX
      A(IL)=X
  115 IF(MV-1) 120,125,120
  120 ILR=ILQ+I
      IMR=IMQ+I
      X=R(ILR)*COSX-R(IMR)*SINX
      R(IMR)=R(ILR)*SINX+R(IMR)*COSX
      R(ILR)=X
  125 CONTINUE
      X=2.0*A(LM)*SINCS
      Y=A(LL)*COSX2+A(MM)*SINX2-X
      X=A(LL)*SINX2+A(MM)*COSX2+X
      A(LM)=(A(LL)-A(MM))*SINCS+A(LM)*(COSX2-SINX2)
      A(LL)=Y
      A(MM)=X

C         TESTS FOR COMPLETION
C
C         TEST FOR M = LAST COLUMN
C

  130 IF(M-N) 135,140,135
  135 M=M+1
      GO TO 60

C         TEST FOR L = SECOND FROM LAST COLUMN
C

  140 IF(L-(N-1)) 145,150,145
  145 L=L+1
      GO TO 55
  150 IF(IND-1) 160,155,160
  155 IND=0
      GO TO 50

C         COMPARE THRESHOLD WITH FINAL NORM
C

  160 IF(THR-ANRMX) 165,165,45

C         SORT EIGENVALUES AND EIGENVECTORS
C

  165 IQ=-N
      DO 185 I=1,N
      IQ=IQ+N
      LL=I+(I*I-I)/2
      JQ=N*(I-2)
```

SUBROUTINE EIGEN ...(CONT'D)

```
      DO 185 J=I,N
      JQ=JQ+N
      MM=J+(J*J-J)/2
      IF(A(LL)-A(MM)) 170,185,185
  170 X=A(LL)
      A(LL)=A(MM)
      A(MM)=X
      IF(MV-1) 175,185,175
  175 DO 180 K=1,N
      ILR=IQ+K
      IMR=JQ+K
      X=R(ILR)
      R(ILR)=R(IMR)
  180 R(IMR)=X
  185 CONTINUE
      RETURN
      END
```

SUBROUTINE TMDEF

```
      SUBROUTINE TMDEF(B,V,G,T,TT,Q1,R,TS,DR,CP,DTM,IA,N,A
     *,TC2)
C
C         THIS SUBROUTINE CALCULATES THE INITIAL VALUE
C         CONTRIBUTION
C         TO THE TEMPERATURE DISTRIBUTION IN THE SOLID
C         PARTICLES.
C         IT ALSO INTEGRATES THE TEMPERATURE DISTRIBUTION
C         THROUGHOUT
C         THE ENTIRE VOLUME OF THE PARTICLES IN ORDER TO
C         OBTAIN THE
C         HEAT RECEIVED BY THE PARTICLES.
C
C     DOUBLE PRECISION Y

      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION TT(12),R(12),Y(12)
      DIMENSION B(12,12),G(12,12),V(12,12),T(200,12)
      DIMENSION UO(12),      TC1(12),TC2(12),         A(78)
     *,TC(12)


      FIF=160.0
      IP=IA
      DO 10 I=1,N
      UO(I)=T(IA,I)
   10 CONTINUE
      CALL GMVRD(V,UO,TC1,N,N,1)
      DO 19 I=1,N
      ECT=A(I)*DTM
      IF(ECT-FIF)39,39,33
   39 ECT= EXP(ECT)
      GO TO 34
   33 ECT=0.0
   34 TC1(I)=TC1(I)*ECT
      TC(I)=TC1(I)+TC2(I)
   19 CONTINUE
      CALL GMVRD(B,TC,TT,N,N,1)
      IP=IP+1
      DO 73 I=1,N
      T(IP,I)=TT(I)
   73 CONTINUE
      DO 57 K=1,N
      Y(K)=(T(IP,K)-T(IA,K))*R(K)*R(K)
   57 CONTINUE
      A21=DR*2.0*(Y(1)+4.0*Y(3)+Y(5))/3.0
      A22=DR*(Y(1)+4.0*Y(2)+2.0*Y(3)+4.0*Y(4)+Y(5))/3.0
      A23=(A22-A21)/15.0
      SB=A22+A23
```

SUBROUTINE TMDEF ...(CONT'D)

```
Q1=CP*SB
TS=TT(N)
RETURN
END
```

SUBROUTINE SIMPS

```
      SUBROUTINE SIMPS(N,F,P,DTM,A,TC2,G)
C
C        THIS SUBROUTINE CALCULATES THE BOUNDARY VALUE
C        CONTRIBUTION
C        TO THE TEMPERATURE DISTRIBUTION IN THE SOLID
C        PARTICLES
C
      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION G(12,12),A(78),TC2(12)
      FIF=160.0
      DO 211 I=1,N
      ECT=A(I)*DTM
      IF(ECT-FIF)39,39,33
   39 ECT= EXP(ECT)
      GO TO 38
   33 ECT=0.0
   38 EPT=ECT-1.0
      BC=((P+F/A(I))*EPT-F*DTM)*G(I,5)/A(I)*81.0
      TC2(I)=BC
  211 CONTINUE
      RETURN
      END
```

SUBROUTINE GMPRD

```
      SUBROUTINE GMPRD(X,Y,Z,L,M,ML)
C          THIS SUBROUTINE MULTIPLIES TWO MATRICES.
C

      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION X(12,12),Y(12,12),Z(12,12)


      DO 21 I=1,L
      DO 21 J=1,L
      SUM=0.0
      DO 22 K=1,L
      SUM=SUM+X(I,K)*Y(K,J)
   22 CONTINUE
      Z(I,J)=SUM
   21 CONTINUE
      RETURN
      END
```

SUBROUTINE GMVRD

```
      SUBROUTINE GMVRD(X,Y,Z,L,M,ML)
C        THIS SUBROUTINE MULTIPLIES A VECTOR WITH A MATRIX.
C
      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION X(12,12),Y(12),Z(12)


      DO 23 I=1,L
      SUM=0.0
      DO 24 K=1,L
      SUM=SUM+X(I,K)*Y(K)
   24 CONTINUE
      Z(I)=SUM
   23 CONTINUE
      RETURN
      END
```

SUBROUTINE GENER

```
      SUBROUTINE GENER(TY,D,W,AA,EA,XO,DZ,MM,M,P,F,DC,STG
     *,TW)
C         THIS SUBROUTINE SOLVES THE GAS PHASE EQUATIONS BY
C         RUNGE-KUTTA METHOD.
C
      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      REAL KP
      DIMENSION TY(8),D(8),W(8),AA(8),EA(8)
      DIMENSION DE(8),KP(4,8)


      DO 101 II=1,4
      GOTO(102,103,104,105),II
  102 XL=XO
      DO 106 I=1,MM
  106 D(I)=TY(I)
      GO TO 107
  103 XL=XO+0.5*DZ
      DO 108 I=1,MM
  108 D(I)=TY(I)+0.5*KP(1,I)
      GO TO 107
  104 DO 109 I=1,MM
  109 D(I)=TY(I)+KP(2,I)
      GO TO 107
  105 XL=XO+DZ
      DO 110 I=1,MM
  110 D(I)=TY(I)+KP(3,I)
  107 CALL SLOPE(D,W,AA,EA,XL,DE,P,F,DC,STG,TW,M)
      DO 101 I=1,MM
  101 KP(II,I)=DZ*DE(I)
      DO 100 I=1,MM
  100 D(I)=TY(I)+(KP(1,I)+KP(4,I)+2.0*(KP(2,I)+KP(3,I)))/6.0
      RETURN
      END
```

SUBROUTINE SLOPE

```
      SUBROUTINE SLOPE(D,W,AA,EA,XL,DE,P,F,DC,STG,TW,M)
C         THIS SUBROUTINE CALCULATES THE FUNCTIONS.
C

      COMMON A1,A2,A3,A4,C,TB,GC,GD,DRR,FR
      COMMON F1,F2,F3,F5,FF1,B2,B5,B6,CAO,CBO
      DIMENSION D(8),W(8),AA(8),EA(8),DE(8),QR(8)


      XQ=XL/10.0
      TW=A1+A2*XQ+A3*XQ**2+A4*XQ**3
      TG=D(4)*TB
      DO 10 I=1,M
   10 QR(I)=W(I)*EXP(AA(I)-EA(I)*C/TG)
      C1=QR(1)*(1.0-D(1))*(1.0-D(2))
      C3=QR(2)*(1.0-D(2))*D(3)
      C7=QR(3)*(1.0-D(1))
      DE(1)=B2*(C1*CBO*(1.0+2.0*CAO*C7)+C3*C7*CAO*CBO)
      DE(2)=B2*(2.0*C1*CAO+C3*CAO)*(1.0+C7*CAO)
      DE(3)=B2*(C1*CBO*(1.0+2.0*CAO*C7)+C3*CBO*(C7*CAO-1.0))
      DE(4)=-F1*(D(4)-TW)-F2*F5*(D(4)-P/TB-F/TB*0.5*DC)+F3
     **DE(2)
      DE(5)=F5*(D(4)-D(5))
      DE(6)=FF1*(D(7)-D(6))/D(6)
      DE(6)=DE(6)+GC/D(6)
      B6=STG*D(6)/(GD*D(4)*TB)
      B5=GD*D(4)*DRR*TB
      CM=DE(4)/D(4)+ B6*DE(6)+2.0*D(7)**2*FR/B5
      CM=CM+(1.0+STG)/(GD*D(4)*TB)
      DN=1.0/D(7)-D(7)/(GD*D(4)*TB)
      DE(7)=CM/DN
      RETURN
      END
```

```
        5        180          3          5          7          5          1
        1          1          1          5          5         60        0.0
   50.000   1545.000     32.200      0.001      9.000      0.625
 1190.000    150.000    150.000      0.050    506.000   1140.000

                         KINETIC PARAMETERS

              48.00000      34.50000       0.00010
              25.00000      35.20000       0.00010
             -25.00000       9.90000       0.00010

                              MATRIX G

   0.16666        0.0            0.0            0.0            0.0
   0.0            4.33330        0.0            0.0            0.0
   0.0            0.0           16.33330        0.0            0.0
   0.0            0.0            0.0           36.33330        0.0
   0.0            0.0            0.0            0.0           64.33330

                              MATRIX B

  -1.00000        1.00000        0.0            0.0            0.0
   1.00000      -10.00000        9.00000        0.0            0.0
   0.0            9.00000      -34.00000       25.00000        0.0
   0.0            0.0           25.00000      -74.00000       49.00000
   0.0            0.0            0.0           49.00000     -130.00000

                      INITIAL CONDITION VECTOR

  1140.00000     1140.00000     1140.00000     1140.00000     1140.00000

                      BOUNDARY CONDITION VECTOR

   0.0            0.0            0.0            0.0
```

```
                              MATRIX K

  -6.000241       1.176725       0.0            0.0            0.0
   1.176725      -2.307711       1.069784       0.0            0.0
   0.0            1.069784      -2.081636       1.026243       0.0
   0.0            0.0            1.026243      -2.036697       1.013504
   0.0            0.0            0.0            1.013504      -2.020724

                              EIGENVALUES

  -0.379675      -1.379019      -2.637214      -3.684029      -6.367013

                              EIGENVECTORS

   0.079721      -0.151063       0.194053      -0.166582       0.951534
   0.390786      -0.593252       0.554592      -0.327891      -0.296591
   0.598587      -0.348836      -0.384280       0.605085       0.078768
   0.595777       0.379596      -0.370077      -0.602999      -0.019745
   0.367949       0.599541       0.608392       0.367423       0.004604

GAS PHASE CONSTANTS

    12.00000        50.00000      1190.00000     1140.00000

PROPERTIES OF SOLID PARTICLES

   197.00000         0.20000         9.00000

POLYNOMIAL COEFFICIENTS FOR WALL TEMPERATURE

     0.99939        -0.27840         1.59250        -1.30014

PARTICLE DIAMETER = 100.00   LOADING RATIO =  5.0   SCALING FACTOR =     9.0

INITIAL CONDITION FOR GAS PHASE EQUATIONS

   0.0        0.0        0.0        1.0000     0.9500     8.8000     7.9950
```

```
                 PARTICLE DIAMETER = 100.00    LOADING RATIO =  5.0

     XA          XB          XC          VG          VP          TG         DL

    T(1)        T(2)        T(3)        T(4)        T(5)        TS         DIF

    0.0         0.0         0.0         7.995       8.800     730.0000     0.0
 680.0000    680.0000    680.0000    680.0000    680.0000    680.0000    50.0000
    0.00009     0.00038     0.00009     7.843       9.069     707.3618     0.500
 700.1086    700.1152    700.1238    700.1299    700.1328    700.1328     7.2290
    0.00036     0.00145     0.00036     7.838       9.094     706.6128     1.000
 704.0925    704.0991    704.1069    704.1118    704.1125    704.1108     2.5020
    0.00112     0.00452     0.00110     7.852       9.105     708.6499     1.500
 706.3340    706.3408    706.3486    706.3535    706.3542    706.3521     2.2979
    0.00325     0.01316     0.00321     7.884       9.127     713.5244     2.000
 709.4758    709.4824    709.4910    709.4961    709.4978    709.4961     4.0233
    0.00904     0.03663     0.00891     7.950       9.171     723.3735     2.500
 715.4236    715.4302    715.4387    715.4448    715.4482    715.4485     7.9250
    0.02344     0.09520     0.02309     8.075       9.257     741.8787     3.000
 726.8057    726.8132    726.8237    726.8313    726.8372    726.8411    15.0376
    0.05334     0.21725     0.05237     8.279       9.408     772.3000     3.500
 746.7075    746.7156    746.7268    746.7373    746.7466    746.7546    25.5454
    0.09913     0.40565     0.09685     8.530       9.618     809.6658     4.000
 775.8257    775.8342    775.8472    775.8601    775.8728    775.8853    33.7805
    0.14795     0.60863     0.14375     8.742       9.836     841.2300     4.500
 808.4939    808.5029    808.5166    808.5300    808.5422    808.5544    32.6755
    0.18621     0.76932     0.18010     8.872      10.000     860.5500     5.000
 835.9434    835.9512    835.9639    835.9753    835.9846    835.9929    24.5571
    0.21074     0.87307     0.20321     8.943      10.101     871.0906     5.500
 855.2561    855.2642    855.2751    855.2839    855.2905    855.2954    15.7952
    0.22478     0.93275     0.21638     8.988      10.162     877.8010     6.000
 867.8108    867.8186    867.8286    867.8359    867.8403    867.8418     9.9592
    0.23236     0.96506     0.22345     9.022      10.203     882.8320     6.500
 875.9878    875.9949    876.0044    876.0115    876.0139    876.0142     6.8179
    0.23632     0.98203     0.22715     9.048      10.233     886.6951     7.000
 881.7234    881.7305    881.7405    881.7466    881.7485    881.7473     4.9478
    0.23837     0.99080     0.22905     9.063      10.254     888.9502     7.500
 885.6643    885.6721    885.6812    885.6875    885.6887    885.6863     3.2635
    0.23942     0.99530     0.23003     9.062      10.262     888.6868     8.000
 887.6091    887.6165    887.6250    887.6306    887.6311    887.6274     1.0593
    0.23956     0.99589     0.23016     9.058      10.262     888.2363     8.100
 887.6882    887.6956    887.7034    887.7083    887.7080    887.7043     0.5320
```

```
                PARTICLE DIAMETER = 200.00   LOADING RATIO =   5.0

         XA            XB            XC           VG          VP         TG          DL

        T(1)          T(2)          T(3)         T(4)        T(5)        TS          DIF

        0.0           0.0           0.0         7.995       8.800     730.0000     0.0
     680.0000      680.0000      680.0000     680.0000    680.0000    680.0000     50.0000
      0.00010       0.00040       0.00010       7.894       9.887     714.9316     0.500
     690.8000      690.8076      690.8193     690.8313    690.8425    690.8538     24.0779
      0.00037       0.00151       0.00037       7.855      10.426     709.2112     1.000
     695.7332      695.7400      695.7500     695.7581    695.7642    695.7693     13.4419
      0.00116       0.00469       0.00115       7.853      10.698     708.8123     1.500
     698.7141      698.7212      698.7310     698.7383    698.7424    698.7456     10.0667
      0.00337       0.01364       0.00333       7.888      10.848     714.0493     2.000
     701.5530      701.5598      701.5696     701.5776    701.5828    701.5872     12.4622
      0.00934       0.03786       0.00921       7.974      10.954     726.8984     2.500
     705.6917      705.6992      705.7112     705.7214    705.7312    705.7395     21.1589
      0.02405       0.09771       0.02367       8.137      11.068     751.1665     3.000
     712.6042      712.6133      712.6279     712.6433    712.6594    712.6765     38.4900
      0.05401       0.22035       0.05294       8.397      11.224     789.8145     3.500
     724.7339      724.7434      724.7632     724.7869    724.8147    724.8467     64.9678
      0.09898       0.40636       0.09637       8.704      11.435     835.5613     4.000
     743.6829      743.6953      743.7205     743.7537    743.7937    743.8425     91.7188
      0.14643       0.60541       0.14151       8.945      11.668     871.4141     4.500
     767.8730      767.8867      767.9150     767.9534    768.0020    768.0601    103.3540
      0.18380       0.76414       0.17657       9.069      11.870     889.9011     5.000
     792.4910      792.5042      792.5317     792.5681    792.6128    792.6670     97.2341
      0.20812       0.86823       0.19920       9.116      12.014     896.7876     5.500
     814.1538      814.1663      814.1909     814.2231    814.2615    814.3074     82.4802
      0.22231       0.92916       0.21234       9.136      12.107     899.8403     6.000
     831.9885      832.0002      832.0215     832.0488    832.0801    832.1172     67.7231
      0.23010       0.96269       0.21954       9.156      12.168     902.7979     6.500
     846.4778      846.4888      846.5085     846.5325    846.5591    846.5889     56.2090
      0.23424       0.98056       0.22336       9.177      12.211     905.9199     7.000
     858.4922      858.5024      858.5198     858.5400    858.5625    858.5869     47.3330
      0.23641       0.98992       0.22535       9.190      12.242     907.7981     7.500
     868.3997      868.4092      868.4250     868.4426    868.4600    868.4795     39.3186
      0.23754       0.99479       0.22638       9.181      12.261     906.5339     8.000
     876.2117      876.2212      876.2356     876.2498    876.2632    876.2764     30.2576
      0.23812       0.99731       0.22692       9.139      12.260     900.2534     8.500
     881.4949      881.5034      881.5156     881.5256    881.5334    881.5393     18.7141
55.858 RC=0
```

```
                PARTICLE DIAMETER = 300.00   LOADING RATIO =  5.0

         XA          XB          XC          VG          VP          TG          DL
        T(1)        T(2)        T(3)        T(4)        T(5)        TS          DIF

         0.0         0.0         0.0        7.995       8.300     730.0000      0.0
     680.0000    680.0000    680.0000    680.0000    680.0000    680.0000     50.0000
      0.00010     0.00041     0.00010       7.917      10.149     718.3623      0.500
     686.6074    686.6167    686.6311    686.6482    686.6667    686.6870     31.6753
      0.00038     0.00154     0.00038       7.868      11.018     711.1460      1.000
     690.2295    690.2373    690.2493    690.2615    690.2729    690.2847     20.8613
      0.00117     0.00476     0.00116       7.857      11.585     709.4321      1.500
     692.6042    692.6121    692.6230    692.6340    692.6433    692.6526     16.7795
      0.00341     0.01381     0.00337       7.894      11.969     714.9829      2.000
     694.8340    694.8423    694.8547    694.8665    694.8772    694.8879     20.0950
      0.00943     0.03826     0.00930       7.997      12.249     730.3301      2.500
     697.8325    697.8416    697.8564    697.8723    697.8892    697.9080     32.4221
      0.02417     0.09828     0.02377       8.194      12.486     759.5466      3.000
     702.1116    702.1211    702.1389    702.1609    702.1958    702.2151     57.3335
      0.05383     0.21997     0.05267       8.502      12.725     805.4622      3.500
     709.2380    709.2502    709.2761    709.3105    709.3530    709.4048     96.0574
      0.09781     0.40290     0.09490       8.868      12.993     859.9858      4.000
     720.7498    720.7661    720.8054    720.8608    720.9324    721.0215    138.9644
      0.14397     0.59861     0.13829       9.169      13.276     904.7522      4.500
     737.3613    737.3809    737.4275    737.4958    737.5864    737.6997    167.0525
      0.18047     0.75619     0.17189       9.343      13.541     930.5681      5.000
     755.9929    756.0134    756.0630    756.1360    756.2327    756.3538    174.2144
      0.20449     0.86122     0.19369       9.423      13.761     942.5264      5.500
     774.4011    774.4209    774.4690    774.5400    774.6335    774.7502    167.7761
      0.21874     0.92391     0.20651       9.465      13.934     948.8191      6.000
     791.5173    791.5366    791.5820    791.6484    791.7354    791.8438    150.9753
      0.22670     0.95912     0.21363       9.500      14.068     953.9397      6.500
     807.1509    807.1697    807.2122    807.2739    807.3545    807.4543    146.4854
      0.23101     0.97827     0.21747       9.531      14.174     958.5190      7.000
     821.4392    821.4568    821.4976    821.5547    821.6289    821.7200    136.7991
      0.23332     0.98852     0.21951       9.547      14.256     961.0144      7.500
     833.5640    833.5796    833.6135    833.6616    833.7234    833.7991    127.2153
      0.23454     0.99395     0.22060       9.535      14.316     959.0920      8.000
     844.1970    844.2117    844.2432    844.2871    844.3411    844.4075    114.6846
      0.23518     0.99682     0.22117       9.476      14.350     950.4001      8.500
     853.2158    853.2292    853.2559    853.2922    853.3367    853.3901     97.0100
92.031 RC=0
```

```
                 PARTICLE DIAMETER = 400.00    LOADING RATIO =   5.0

          XA          XB          XC          VG          VP          TG          DL

        T(1)        T(2)        T(3)        T(4)        T(5)          TS         DIF

         0.0         0.0         0.0       7.995       8.800   730.0000        0.0
    680.0000    680.0000    680.0000    680.0000    680.0000   680.0000    50.0000
     0.00010     0.00041     0.00010       7.927      10.262   719.9412      0.500
    684.3848    684.3945    684.4124    684.4331    684.4575   684.4846    35.4565
     0.00038     0.00155     0.00038       7.874      11.305   712.0591      1.000
    687.0212    687.0295    687.0432    687.0593    687.0764   687.0945    24.9646
     0.00118     0.00479     0.00117       7.859      12.062   709.7644      1.500
    688.8621    688.8701    688.8835    688.8975    688.9114   688.9265    20.8379
     0.00343     0.01389     0.00339       7.899      12.625   715.6643      2.000
    690.6008    690.6096    690.6235    690.6396    690.6563   690.6746    24.9897
     0.00947     0.03843     0.00934       8.013      13.064   732.6465      2.500
    692.7612    692.7703    692.7866    692.8057    692.8254   692.8479    39.7986
     0.02419     0.09842     0.02379       8.230      13.434   764.9302      3.000
    695.7351    695.7461    695.7686    695.7974    695.8330   695.8752    69.0549
     0.05361     0.21933     0.05240       8.568      13.778   815.2957      3.500
    700.5476    700.5625    700.5952    700.6414    700.6987   700.7705   114.5251
     0.09695     0.40027     0.09383       8.972      14.127   875.3987      4.000
    708.0854    708.1042    708.1504    708.2183    708.3079   708.4197   166.9790
     0.14229     0.59398     0.13609       9.314      14.478   926.3306      4.500
    718.4517    718.4749    718.5322    718.6204    718.7388   718.8877   207.4429
     0.17820     0.75097     0.16866       9.527      14.809   957.9844      5.000
    730.6335    730.6594    730.7239    730.8230    730.9558   731.1233   226.8611
     0.20196     0.85666     0.18978       9.639      15.101   974.6284      5.500
    743.3123    743.3379    743.4033    743.5044    743.6401   743.8125   230.8159
     0.21616     0.92048     0.20222       9.703      15.348   984.2273      6.000
    755.7063    755.7322    755.7974    755.8965    756.0300   756.1987   228.0286
     0.22418     0.95677     0.20918       9.752      15.555   991.4041      6.500
    767.5496    767.5742    767.6360    767.7312    767.8591   768.0208   223.3833
     0.22857     0.97676     0.21297       9.789      15.728   996.9072      7.000
    778.7632    778.7874    778.8474    778.9385    779.0615   779.2163   217.6909
     0.23094     0.98758     0.21500       9.804      15.871   999.1736      7.500
    789.3149    789.3384    789.3953    789.4819    789.5981   789.7441   209.4294
     0.23221     0.99338     0.21609       9.781      15.984   995.7041      8.000
    798.9890    799.0110    799.0645    799.1440    799.2490   799.3811   196.3230
     0.23289     0.99647     0.21669       9.701      16.064   983.7915      8.500
    807.4958    807.5159    807.5632    807.6326    807.7239   807.8381   175.9534
 95.346 RC=0
```

APPENDIX G

PARAMETER ESTIMATION

The steepest descent method due to Rosenbrock was programmed in Fortran IV to solve the problem of finding the characteristic parameter vector $\underline{a}$ of a system of differential equations of the form

$$\frac{d\underline{x}}{dt} = \underline{g}(\underline{x} , \underline{a} , t)$$

It was assumed that n different experiments were performed with the known initial conditions $\underline{x}_j$ (0) j = 1,2,...,n and that some or all of the state variables were measured at several discrete times. Given the model and the data, the parameter vector is found such that the unweighted least squares are minimized.

The Fortran IV program listed on the following pages, is broken up into a main line and five subroutines. The purpose of each subroutine is stated in the comment cards at the beginning. The main line program reads in the data and controls the stepping procedure. Comment cards in the main line program defined each variable which is read in as data. All of the subroutines are general except for the subroutine SLOPE, which defines the functions and hence must be supplied for the functional models being tested. Two models were proposed in the present study for the partial oxidation of n-butane. The models were later used to predict the temperature profiles and conversions for a number of other runs by Anderson(1). The runs used for this purpose were runs 11, 12, 13, 14 and 17 in his work. The experimental results for these runs are given below in Tables G-1 to G-5. The models were also used to predict the overall behaviour of the transported bed reactor.

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It was assumed that n different experiments were performed with the known initial conditions $\underline{x}_j$ (0) j = 1,2,...,n and that some or all of the state variables were measured at several discrete times. Given the model and the data, the parameter vector is found such that the unweighted least squares are minimized.

The Fortran IV program listed on the following pages, is broken up into a main line and five subroutines. The purpose of each subroutine is stated in the comment cards at the beginning. The main line program reads in the data and controls the stepping procedure. Comment cards in the main line program defined each variable which is read in as data. All of the subroutines are general except for the subroutine SLOPE, which defines the functions and hence must be supplied for the functional models being tested. Two models were proposed in the present study for the partial oxidation of n-butane. The models were later used to predict the temperature profiles and conversions for a number of other runs by Anderson(1). The runs used for this purpose were runs 11, 12, 13, 14 and 17 in his work. The experimental results for these runs are given below in Tables G-1 to G-5. The models were also used to predict the overall behaviour of the transported bed reactor.

TABLE G.1

Experimental Results for Run 11

Inlet Composition:	Oxygen 6.3519	Nitrogen 23.8951
	Butane 69.7530	Mole Per Cent
Inlet Temperature:	705°F	
Pressure:	53.50 psia	
Inlet Flow Rate:	11.46 lb/hr	

Length Along Reactor ft	Conversion n-Butane	Conversion Oxygen	Temperature Gas °F	Temperature Wall °F
2.54	0.0702	0.6374	851	1027
3.43			1032	
4.31	0.1670	0.9420	1009	949
5.2			988	
6.1	0.1865	0.9471	964	906
6.9			947	
7.88	0.1974	0.9486	932	883

TABLE G.2

Experimental Results for Run 12

Inlet Composition: Oxygen 6.2946 Nitrogen 23.6798
Butane 70.0256 Mole Per Cent

Inlet Temperature: 704°F

Pressure: 53.50 psia

Inlet Flow Rate: 13.58 lb/hr

Length Along Reactor ft	Conversion $\underline{n}$-Butane	Conversion Oxygen	Temperature Gas °F	Temperature Wall °F
2.54	0.01712	0.2491	698	727
3.43			1023	
4.31	0.1168	0.7810	1036	975
5.2			1013	
6.1	0.1803	0.9485	989	934
6.9			973	
7.88	0.1940	0.9481	959	912

TABLE G.2

Experimental Results for Run 12

Inlet Composition:	Oxygen 6.2946	Nitrogen 23.6798
	Butane 70.0256	Mole Per Cent
Inlet Temperature:	704°F	
Pressure:	53.50 psia	
Inlet Flow Rate:	13.58 lb/hr	

Length Along Reactor ft	Conversion n-Butane	Conversion Oxygen	Temperature Gas °F	Temperature Wall °F
2.54	0.01712	0.2491	698	727
3.43			1023	
4.31	0.1168	0.7810	1036	975
5.2			1013	
6.1	0.1803	0.9485	989	934
6.9			973	
7.88	0.1940	0.9481	959	912

TABLE G.3

Experimental Results for Run 13

Inlet Composition:	Oxygen 6.4688	Nitrogen 24.3352
	Butane 69.1960	Mole Per Cent
Inlet Temperature:	705°F	
Pressure:	53.5 psia	
Inlet Gas Flow Rate:	12.21 lb/hr	

Length Along Reactor ft	Conversion Butane	Conversion Oxygen	Temperature Gas °F	Temperature Wall °F
2.54	0.0740	0.9450	800	1076
3.43			1045	
4.31	0.1436	0.9550	1026	958
5.2			1000	
6.1	0.1919	0.9582	975	913
6.9			940	
7.88	0.2136	0.9577	940	885

TABLE G.4

Experimental Results for Run 14

Inlet Composition:	Oxygen 6.4688	Nitrogen 24.3352
	Butane 69.1960	Mole Per Cent
Inlet Temperature:	696°F	
Reactor Pressure:	53.5 psia	
Inlet Flow Rate:	12.21 lb/hr	

Length Along Reactor ft	Conversion Butane	Conversion Oxygen	Temperature Gas °F	Temperature Wall °F
2.54	0.0151	0.1154	678	705
3.43			896	
4.31	0.1473	0.9082	1040	958
5.2			1015	
6.1	0.1923	0.9507	983	909
6.9			954	
7.88	0.2172	0.9497	941	878

TABLE G.5

Experimental Results for Run 17

Inlet Composition:	Oxygen 7.2378	Nitrogen 27.2277
	Butane 65.5345	Mole Per Cent
Inlet Temperature:	681°F	
Reactor Pressure:	53.5 psia	
Inlet Gas Flow Rate:	12.8 lb/hr	

Length Along Reactor ft	Conversion Butane	Conversion Oxygen	Temperature Gas °F	Temperature Wall °F
2.54	0.0093	0.0302	653	637
3.43			656	
4.31	0.0259	0.2849	697	-
5.2			939	
6.1	0.1640	0.8157	1058	980
6.9			1023	
7.88	0.2068	0.9639	994	916

The computer program with some sample output is now presented.

```
      C         PARAMETER
C         PARAMETER
C         THE PURPOSE OF THIS PROGRAM IS TO IDENTIFY CER-
C         TAIN UNKNOWN PARAMETERS IN A SYSTEM OF ORDINARY
C         DIFFERENTIAL EQUATIONS. THE DIFFERENTIAL EQUA-
C         TIONS REPRESENT A PHYSICAL SYSTEM FROM WHICH
C         EXPERIMENTAL DATA HAS BEEN OBTAINED. ROSENBROCK'S
C         METHOD OF STEEPEST DESCENT METHOD HAS BEEN USED
C         TO ESTIMATE THE PARAMETERS FROM THE GIVEN DATA.
C
C
      COMMON ISTEP,NPITOT,LRT
      COMMON A1(20),A2(20),A3(20),A4(20),A5(20),C6(20)
      COMMON YO2(20),YN2(20),YC4(20),CBT(20),COX(20)
      COMMON WG(20),PR(20),GG(20),NWT,NDS,TB,RR,WM,DRR
      DIMENSION XO(20,8),TC(20,20),XB1(20,20,8),C1(12)
      DIMENSION KS(10),KSF(10),KF(10),NC(20,20)
      DIMENSION NP(20),NPIJ(20,20),NPITOT(20),KSI(20,20,8)
      DIMENSION DS(10),WT(10),STM(20)
      DIMENSION PRE(20,20,8)
      DOUBLE PRECISION ELAM(10),OV(10,10),PAR1(10),PAR3(10)
      DOUBLE PRECISION SS,VAR1,VAR3,CT,VAR2
      DOUBLE PRECISION SMXMN
C        IN ORDER TO USE THIS PROGRAM, THE DIFFERENTIAL
C        EQUATION MUST BE NORMALISED SUCH THAT
C      1 THE STATE VARIABLES DO NOT DIFFER BY MORE THAN
C        AN ORDER OF MAGNITUDE.
C      2 THE INDEPENDENT VARIABLES VARIES FROM ZERO TO A
C        VALUE NOT EXCEEDING 10, WITH THE INITIAL CONDITION
C        BEING GIVEN AT ZERO.
C      3 THE ELEMENTS OF THE PARAMETER VECTOR  ARE OF THE
C        SAME ORDER OF MAGNITUDE.
C
C
C        THE MAIN LINE PROGRAM HAS THE FUNCTIONS OF READING
C        IN THE DATA SETS, DETERMINE THE SUCCESS/FAILURE
C        OF EACH STEP IN RIDGE TRACKING, DETERMINE THE STEP
C        SIZE AND DECIDE ON THE ROTATION OF AXES.
C        THE AUXILLIARY SUBROUTINES REQUIRED ARE
C       VARIA-
C        GENERATE THE SOLUTION GIVEN THE PARAMETERS.
C       GENER-
C        RUNGE KUTTA METHOD OF INTEGRATION TO SOLVE THE
C        DIFFERENTIAL EQUATIONS.
C       ROTAT-
C        ROTATE THE AXES USING THE GRAM-SCHMIDT ORTHOGONA-
C        LIZATION PROCESS.
C       FORS-
```

```
C         OBTAINS A POLYNOMIAL FOR REACTOR WALL TEMPERA-
C         TURE. USUALLY THIS ROUTINE WAS USED SEPARATELY.
C        SLOPE
C         SUPPLIES THE FUNCTIONS.
C
C

      SMXMN=1.D+0
      READ(5,41)WMO,WN2,WC4,RR,TB,DRR
      DRR=DRR/12.0
      WRITE(6,41)WMO,WN2,WC4,RR,TB,DRR
   41 FORMAT(6F12.5)
      ARR=0.785*DRR**2

C         THE FOLLOWING INTEGERS ARE READ IN ON A 16I5
C         FORMAT.
C
C         NE    THE NO. OF STATE VARIABLES. NE 11
C
C         NK    THE NO. OF PARAMATERS. NK 11
C
C
C         NDS   THE NO. OF DATA SETS. NDS 21
C         MAXR   MAXIMUM NUMBER OF TRIALS
C
C         MAXS   MAXIMUM NUMBER OF STAGES
C
C         NW     NUMBER OF DATA POINTS GIVEN FOR WALL
C         TEMPERATURE
C
C         MF     ORDER OF POLINOMIALS FOR WALL TEMPERATURE
C         PROFILE
C
C
C

      READ(5,1)NE,NK,NDS,MAXR,MAXS,NW,MF
      WRITE(6,1)NE,NK,NDS,MAXR,MAXS,NW,MF

C
C        PAR1  THE INITIAL GUESS FOR THE PARAMETER VECTOR IS
C              READ IN ON A 5E16.6 FORMAT.
C
C

      READ(5,41)(PAR1(I),I=1,NK)
      WRITE(6,11)(PAR1(I),I=1,NK)

C
C         THE FOLLOWING CONTROL VARIABLES ARE READ IN ON A
```

```
          C          PARAMETER         ...(CONT'D)
C         4E16.6 FORMAT.
C
C         KPN   NORMALIZATION FLAG FOR PARAMETER VECTOR
C         KPN=0   NORMALIZATION DESIRED
C         KPN=-1  NORMALIZATION NOT DESIRED
C
C
C         NWT   WALL TEMPERATURE FLAG
C         NWT=0     NON ADIABATIC, WALL TEMPERATURES GIVEN
C         NWT=1     ADIABATIC
C
      READ(5,12)SS,KPN,NWT
      WRITE(6,12)SS,KPN,NWT
   11 FORMAT(5E16.6)
   12 FORMAT(E16.6,5X,2I5)
      NPTOT=0
C
C         THE DATA FOR EACH EXPERIMENT ARE READ IN
C         SEQUENTIALLY AS GIVEN BELOW. ALL INTEGERS ARE READ
C         IN ON A 16I5 FORMAT AND ALL OTHER DATA ON A 8F10.6
C         FORMAT. THE DATA IS PRINTED OUT EXACTLY AS IT IS
C         READ IN.
C
C         T IS THE INDEPENDENT VARIABLE.
C
C
      DO 101 I=1,NDS


      READ(5,1)NRUN
      WRITE(6,1)NRUN
      READ(5,18)A1(I),A2(I),A3(I),A4(I)
   18 FORMAT(4F15.0)
      WRITE(6,23)A1(I),A2(I),A3(I),A4(I)
   23 FORMAT(10X,4F12.6)
      READ(5,11)WG(I),PR(I),STM(I),YO2(I)
      WRITE(6,11)WG(I),PR(I),STM(I),YO2(I)
      READ(5,19)YN2(I),YC4(I)
      WRITE(6,19)YN2(I),YC4(I)
   19 FORMAT(2E16.6)
      WM=YO2(I)*WMO+YN2(I)*WN2+YC4(I)*WC4
      WG(I)=WG(I)/ARR
      GG(I)=WG(I)/WM
      DG=(WM*PR(I))/(10.73*STM(I))
      CBT(I)=YC4(I)*DG/WM
      COX(I)=YO2(I)*DG/WM
```

```
                C          PARAMETER        ...(CONT'D)
C         XO(I,J) THE INTIAL CONDITION FOR THE J TH STATE
C              VARIABLE FOR THE I TH EXPERIMENT.
C

      READ(5,2) (XO(I,J),J=1,NE)
      WRITE(6,2)(XO(I,J),J=1,NE)
      XO(I,NE)=(XO(I,NE)+460.0)/1185.0

C         NP(I) THE NO. OF VALUES OF T FOR WHICH DATA ARE
C              GIVEN IN THE I TH EXPERIMENT.
C

      READ(5,1) NP(I)
      WRITE(6,1)NP(I)
      M1=NP(I)

C         NPIJ(I,J) THE NO. OF DATA POINTS WHICH ARE GIVEN
C              FOR THE J TH VALUE OF T FOR WHICH DATA ARE
C              GIVEN FOR THE I TH EXPERIMENT.
C

      READ(5,1) (NPIJ(I,J),J=1,M1)
      WRITE(6,1)(NPIJ(I,J),J=1,M1)

C         TC(I,J) THE VALUE OF THE J TH VALUE OF T FOR WHICH
C              DATA ARE GIVEN FOR THE I TH EXPERIMENT.
C

      READ(5,2) (TC(I,J),J=1,M1)
      WRITE(6,2)(TC(I,J),J=1,M1)

C         NC(I,J) THE NO. OF INTEGRATION POINTS REQUIRED
C              BETWEEN TC(I,J) AND TC(I-1,J) WITH TC(0,J)
C              BEING TAKEN AS ZERO.
C

      READ(5,1) (NC(I,J),J=1,M1)
      WRITE(6,1)(NC(I,J),J=1,M1)
      NPITOT(I)=0
      DO 100 J=1,M1
      M2=NPIJ(I,J)
      NPITOT(I)=NPITOT(I)+M2

C         KSI(I,J,K) THE STATE VARIABLE INDEX OF THE K TH
C              DATA POINT AT TC(I,J).
C

      READ(5,1) (KSI(I,J,K),K=1,M2)
      WRITE(6,1)(KSI(I,J,K),K=1,M2)
```

```
          C          PARAMETER       ...(CONT'D)
C
C         XB1(I,J,K) THE VALUE OF THE K TH DATA POINT AT
C              TC(I,J) WITH THE INDEX KSI(I,J,K).
C

      READ(5,2) (XB1(I,J,K),K=1,M2)
      WRITE(6,3)(XB1(I,J,K),K=1,M2)
      XB1(I,J,M2)=(XB1(I,J,M2)+460.0)/1185.0
  100 CONTINUE
  101 NPTOT=NPTOT+NPITOT(I)
C
C         THE TOTAL NO. OF DATA POINTS IS WRITEN OUT.
C
C

      WRITE(6,22) NPTOT
   22 FORMAT('0THE TOTAL NO. OF DATA POINTS IS ',I5)
    1 FORMAT(16(1X,I4))
    2 FORMAT(8F10.5)
    3 FORMAT(1X,8F10.5)
C
C         IF THE TOTAL NO. OF DATA POINTS EXCEEDS 500 THEN
C         THE PROGRAM IS TERMINATED.
C
C

      IF(NPTOT.LE.500) GOTO 120
      WRITE(6,21)
   21 FORMAT('0NO. OF DATA POINTS EXCEEDS 500')
      STOP
C
C
C         GENERATE INITIAL SET OF ORTHOGONAL VECTORS AND
C         NULL SCALING FACTORS
C        PAR3  VECTOR TO STORE THE PARAMETERS
C

  120 WRITE(6,403)
  403 FORMAT(1H1)
  173 DO 5 I=1,NK
      KSF(I)=0
    5 PAR3(I)=PAR1(I)
   14 DO 67 I=1,NK
      DO 6 J=1,NK
    6 OV(I,J)=0.0D+00
   67 OV(I,I)=1.0D+00
      LRT=0
      ISTEP=0
```

```
          C           PARAMETER        ...(CONT'D)

C          CALCULATION OF FUNCTION VALUE FOR INITIAL GUESSES
C

      CALL VARIA(NE,NK,PRE,NC,KSI,NP,NPTOT,PAR1,XB1,XO,VAR2
     *,TC,NPIJ)
      LRT=-1

C          VAR3  VECTOR TO STORE THE VARIANCE/

      VAR2=VAR2*SMXMN
      VAR1=VAR2
      VAR3=VAR1
      WRITE(6,531)VAR3
  531 FORMAT(5X,41HVARIANCE WITH INITIAL PARAMETER VALUES =
     *,D18.8)

C          COMMENCE ROSENBROCK ALGORITHM
C

      DO 7 KKK=1,MAXS
      WRITE(6,303)KKK
  303 FORMAT(10X,11HBEGIN STAGE,I3)

C          GENERATE INITIAL STEPSIZES AND SUCCESS/FAILURE
C          FLAGS
C

      DO 85 I=1,NK
      ELAM(I)=SS*(10.D+00)**KSF(I)
      KS(I)=1
   85 KF(I)=1

C          COMMENCE RIDGE TRACKING
C

      DO 80 KLP=1,MAXR
      IF(KLP.EQ.MAXR)GOTO579
      ISTEP=ISTEP+1
      DO 90 II=1,NK

C          ADJUSTMENT OF PARAMETERS
C

   93 DO 9 I=1,NK
    9 PAR1(I)=PAR1(I)+OV(II,I)*ELAM(II)

C          CALCULATE NEW FUNCTION VALUE AND COMPARE TO OLD
C          ONE
C
```

```
C          PARAMETER       ...(CONT'D)

      CALL VARIA(NE,NK,PRE,NC,KSI,NP,NPTOT,PAR1,XB1,XO,VAR2
     *,TC,NPIJ)
      VAR2=VAR2*SMXMN
      IF(LRT.EQ.0) GO TO 95
      GO TO 94
   95 WRITE(6,535) VAR2
  535 FORMAT(9X,11HVARIANCE = ,D18.5)
   94 LRT=-1
      IF(VAR1-VAR2) 10,203,203

C          SUCCESSFUL STEP, ADUST STEPSIZE AND SET SUCCESS
C          FLAG
C

  203 VAR1=VAR2
      ELAM(II)=ELAM(II)*3.0D+00
      IF(KS(II))89,81,89
   89 KS(II)=0
      GO TO 81

C          UNSUCCESSFUL STEP, RETURN TO PREVIOUS PARAMETER
C          VALUES, ADJUST STEPSIZE AND DIRECTION AND SET
C          FAILURE FLAG
C

   10 DO 13 I=1,NK
      PAR1(I)=PAR1(I)-ELAM(II)*OV(II,I)
   13 CONTINUE
      ELAM(II)=ELAM(II)/(-2.0D+00)
      IF(KS(II))81,91,81
   91 KS(II)=-1

C          TEST FOR OSCILLATORY STEPPING STATUS AND MAGNITUDE
C          OF STEPSIZE
C

   81 DO 82 I=1,NK
  505 IF(KS(I))82,90,90
   82 CONTINUE
      GO TO 83
   90 CONTINUE
   80 CONTINUE
   83 CONTINUE

      ISTEP=0

C          ROTATION OF AXES
C
```

```
C              PARAMETER            ...(CONT'D)
      CALL ROTAN(NK,PAR1,PAR3,OV)


      DO 40 I=1,NK
      PAR1(I)=PAR1(I)/((10.D+00)**KSF(I))
   40 CONTINUE
      DO 17 I=1,NK
      PAR1(I)=PAR1(I)*((10.D+00)**KSF(I))
   17 PAR3(I)=PAR1(I)
      WRITE(6,591)KKK,(PAR1(I),I=1,NK)
  591 FORMAT(1X,31HPARAMETER VALUES AFTER ROTATION,I4,2X
     *,3HARE//10X,3F10
     2.2)
      IF(DABS(VAR1-VAR3)-1.D-08) 30,30,310
  310 VAR3=VAR1
      IF(KPN)301,30,301
  301 LRT=0
    7 CONTINUE
      WRITE(6,401)KKK
  401 FORMAT(1H,5X,33HTHE SYSTEM DID NOT CONVERGE AFTER,I4
     *,1X,6HSTAGES)
      STOP
   30 IF(KPN-1) 102,209,102
  102 KPN=1
      CALL TORM(NK,PAR1,KSF)
      DO 33 I=1,NK
   33 PAR3(I)=PAR1(I)
      GO TO 14
  209 DO 31 I=1,NK
   31 PAR1(I)=PAR1(I)/((10.D+00)**KSF(I))
      WRITE(6,597)(PAR1(I),I=1,NK)
  597 FORMAT(1H,5X,30HTHE FINAL PARAMETER VALUES ARE//20X
     *,7F8.2)
  300 CONTINUE
  579 WRITE(6,581)KLP
  581 FORMAT(10X,33HTHE SYSTEM DID NOT CONVERGE AFTER,I4,2X
     *,6HTRIALS)
      STOP
      END
```

SUBROUTINE VARIA

```
      SUBROUTINE VARIA(NE,NK,PRE,NC,KSI,NP,NPTOT,CO,XB1,XO
     *,VAR2,TC,NPIJ)
      COMMON ISTEP,NPITOT,LRT
      COMMON A1(20),A2(20),A3(20),A4(20),A5(20),C6(20)
      COMMON YO2(20),YN2(20),YC4(20),CBT(20),COX(20)
      COMMON WG(20),PR(20),GG(20),NWT,NDS,TB,RR,WM,DRR
      DOUBLE PRECISION CO,VAR2,SUMA,SUMB,CF
      DIMENSION CO(10),X(20,8),XBAR(20,20,8),XB1(20,20,8)
      DIMENSION NC(20,20),KSI(20,20,8),NP(40),XO(20,8),TC(20
     *,20)
      DIMENSION NPIJ(20,20),NPITOT(20)
      DIMENSION PRE(20,20,8)
C
C           GENERATE THE SOLUTION FROM THE APPROXIMATE
C           PARAMETERS.
C
C
   95 FORMAT(5X,9HFOR TRIAL,I3,2X,8HDATA SET,I3,2X,4HWITH,I4
     *,2X,6HPOINTS
     2/5X,24HTHE INITIAL CONDITION IS/)
   96 FORMAT(10X,8F10.4)
   97 FORMAT(5X,17HTHE CONSTANTS ARE/10X,9E12.4/)
      SUMB=0.0
      DO 103 I=1,NDS
      INR=I
      IF(LRT)71,72,71
   72 WRITE(6,95)ISTEP,I,NPITOT(I)
      XO(I,NE)=XO(I,NE)*1185.0-460.0
      WRITE(6,96)(XO(I,II),II=1,NE)
      XO(I,NE)=XO(I,NE)/1185.0+460.0/1185.0
      WRITE(6,97)(CO(II),II=1,NK)
   71 T=0.0
      DO 104 II=1,NE
  104 X(1,II)=XO(I,II)
      M1=NP(I)
      DO 103 J=1,M1
      NCJ=NC(I,J)
      F=NCJ
      H=(TC(I,J)-T)/F
      CALL GENER(NE,NK,NCJ,H,T,X,CO,INR)
      M2=NPIJ(I,J)
      DO 105 K=1,M2
      S=KSI(I,J,K)
      XBAR(I,J,K)=X(1,S)
C     SUMA=ABS(XB1(I,J,K)-XBAR(I,J,K))*PRE(I,J,K)

      SUMA=ABS(XB1(I,J,K)-XBAR(I,J,K))
```

SUBROUTINE VARIA ...(CONT'D)

```
      SUMB=SUMB+SUMA**2
  105 CONTINUE
  103 CONTINUE
      NPS=NK+1
      CF=FLOAT(NPTOT-NPS)
      VAR2=SUMB/CF
      RETURN
      END
```

SUBROUTINE GENER

```
      SUBROUTINE GENER(NE,NK,NCJ,H,T,X,PAR1,INR)
C
C          THE PURPOSE OF THIS SUBROUTINE IS TO GENERATE THE
C          SOLUTION OF THE SYSTEM OF DIFFERENTIAL EQUATIONS
C          GIVEN A SET OF PARAMETERS. THE 4 TH ORDER RUNGE
C          KUTTA PROCEEDURE IS USED.
C
C
      COMMON ISTEP,NPITOT,LRT
      COMMON A1(20),A2(20),A3(20),A4(20),A5(20),C6(20)
      COMMON YO2(20),YN2(20),YC4(20),CBT(20),COX(20)
      COMMON WG(20),PR(20),GG(20),NWT,NDS,TB,RR,WM,DRR
      REAL KP
      DOUBLE PRECISION PAR1
      DIMENSION X(20,8),XA(20,8),PAR1(10),KP(4,10),G(10)
     *,NPITOT(20)
C
      DO 300 N=1,NCJ
      DO 101 II=1,4
      GOTO(102,103,104,105),II
  102 TA=T
      DO 106 I=1,NE
  106 XA(1,I)=X(1,I)
      GOTO 107
  103 TA=T+0.5*H
      DO 108 I=1,NE
  108 XA(1,I)=X(1,I)+0.5*KP(1,I)
      GOTO 107
  104 DO 109 I=1,NE
  109 XA(1,I)=X(1,I)+0.5*KP(2,I)
      GOTO 107
  105 TA=T+H
      DO 110 I=1,NE
  110 XA(1,I)=X(1,I)+KP(3,I)
  107 CALL SLOPE(NE,NK,XA,G,PAR1,II,TA,INR)
      DO 101 I=1,NE
  101 KP(II,I)=H*G(I)
      T=TA
      DO 100 I=1,NE
  100 X(1,I)=X(1,I)+(KP(1,I)+2.0*(KP(2,I)+KP(3,I))+KP(4,I))
     */6.0
  300 CONTINUE
      IF(LRT)71,72,71
   72 X(1,NE)=X(1,NE)*1185.0-460.0
      WRITE(6,500)T,(X(1,I),I=1,NE)
      X(1,NE)=X(1,NE)/1185.0+460.0/1185.0
```

SUBROUTINE GENER ...(CONT'D)

```
500 FORMAT(7X,1H*,10F10.4)
 71 RETURN
    END
```

SUBROUTINE ROTAN

```
      SUBROUTINE ROTAN(P,PAR1,PAR3,OV)
C        THIS SUBROUTINE ROTATES THE AXES USING THE GRAM
C        SCHMIDT ORTHOGONALIZATION PROCESS.
C
      COMMON ISTEP,NPITOT,LRT
      COMMON A1(20),A2(20),A3(20),A4(20),A5(20),C6(20)
      COMMON YO2(20),YN2(20),YC4(20),CBT(20),COX(20)
      COMMON WG(20),PR(20),GG(20),NWT,NDS,TB,RR,WM,DRR
      DIMENSION NPITOT(20)
      INTEGER P
      DOUBLE PRECISION S,SO,DOG
      DOUBLE PRECISION A(10,10),B(10,10),PAR1(10),PAR3(10)
     *,OV(10,10)
C
      DO 1 I=1,P
      DO 1 J=1,P
      A(I,J)=0.0D+00
    1 B(I,J)=0.0D+00
      DO 2 I=1,P
      DO 2 J=I,P
      A(I,J)=PAR1(J)-PAR3(J)
    2 B(I,J)=A(I,J)
      SO=0.0D+00
      DO 3 J=1,P
    3 SO=SO+A(1,J)**2
      S=SO**0.5
      DO 4 J=1,P
    4 OV(1,J)=A(1,J)/S
      DO 5 I=2,P
      MI=I-1
      DO 6 K=1,MI
      DOG=0.0D+00
      DO 7 J=1,P
    7 DOG=DOG+OV(K,J)*A(K,J)
      DO 8 J=1,P
    8 B(I,J)=B(I,J)-DOG*OV(K,J)
    6 CONTINUE
      SO=0.0 D+00
      DO 9 J=1,P
    9 SO=SO+B(I,J)**2
      S=SO**0.5
      DO 10 J=1,P
   10 OV(I,J)=B(I,J)/S
    5 CONTINUE
      RETURN
      END
```

SUBROUTINE TORM

```
      SUBROUTINE TORM (P,PAR1,KSF)
C        THIS SUBROUTINE MAPS THE PARAMETERS BETWEEN 0.1
C        AND 1.0
C
      COMMON ISTEP,NPITOT,LRT
      COMMON A1(20),A2(20),A3(20),A4(20),A5(20),C6(20)
      COMMON YO2(20),YN2(20),YC4(20),CBT(20),COX(20)
      COMMON WG(20),PR(20),GG(20),NWT,NDS,TB,RR,WM,DRR
      INTEGER P
      DOUBLE PRECISION PAR1(10),PP1
      DIMENSION KSF(10)
      DIMENSION NPITOT(20)
C
      DO 1 I=1,P
    1 KSF(I)=0
      DO 2 I=1,P
      PP1=DLOG10(PAR1(I))
      IF(PP1) 3,4,4
    3 KSF(I)=PP1-1
      GO TO 2
    4 KSF(I)=PP1
    2 CONTINUE
      RETURN
      END
```

SUBROUTINE FORS

```
      SUBROUTINE FORS(X,Y,N,NN,M,C1)
C FORSYTHE POLYNOMIAL CURVE FIT USING LEAST SQUARE CRITERIA
C
C
C      THE VECTOR C1 CONTAINS THE COEFFICIENTS OF THE POWER
C      SERIES EXPANSION OF THE FORSYTHE POLYNOMIAL FIT.
C      Y=C1(1)+C1(2)*X+C1(3)*X*X+...
C      THERE ARE M+1 COEFFICICIENTS WHERE M IS THE ORDER OF
C      THE FIT
C
      INTEGER N,I,J,M
      INTEGER L ,LL
      REAL P(10,20),X(20),Y(20),F(20),DIFF(20),W(20)
     *,PERER(20)
      REAL A(10),B(10),C(10),S,V,Q,T,STDEV
      REAL D(10,10),C1(10),Z(20)
C      X  DISTANCE ALONG REACTOR  FT
C      Y  TEMPERATURE IN DEGREES RANKINE
C      N  NUMBER OF DATA POINTS
C      M  ORDER OF POLYNOMIAL
C      THE LENGTH AND TEMPERATURE IN THIS PROGRAM ARE
C      NORMALIZED.
C
      DO 10 I=1,N
      F(I)=0.0
      W(I)=1.0
      P(1,I)=1.0
      X(I)=X(I)/10.0
      Y(I)=(Y(I)+460.0)/1185.0
   10 CONTINUE
      B(1)=0.0
      DO 11 J=1,M
      IF(J-1)12,12,31
   31 T=0.0
      DO 13 I=1,N
      T=T+W(I)*X(I)*P(J-1,I)*P(J,I)
   13 CONTINUE
      B(J)=T/V
   12 V=0.0
      S=0.0
      Q=0.0
      DO 14 I=1,N
      V=V+W(I)*P(J,I)**2
      S=S+W(I)*X(I)*P(J,I)**2
      Q=Q+W(I)*Y(I)*P(J,I)
   14 CONTINUE
```

SUBROUTINE FORS ...(CONT'D)

```
      A(J+1)=S/V
      C(J)=Q/V
      DO 15 I=1,N
      IF(J-1)16,16,32
   32 P(J+1,I)=(X(I)-A(J+1))*P(J,I)-B(J)*P(J-1,I)
      GOTO 15
   16 P(J+1,I)=(X(I)-A(J+1))*P(J,I)
   15 CONTINUE
      STDEV=0.0
      DO 17 I=1,N
      F(I)=F(I)+C(J)*P(J,I)
      DIFF(I)=ABS(Y(I)-F(I))
      PERER(I)=100.0*DIFF(I)/Y(I)
      STDEV=STDEV+DIFF(I)**2
   17 CONTINUE
      STDEV=STDEV/FLOAT(N-1)
      STDEV=SQRT(STDEV)
      IF(J-M)11,33,11
   33 WRITE(6,3) J,STDEV
      WRITE(6,4)
      WRITE(6,5) (I,A(I),B(I-1),I=2,J)
      WRITE(6,6)
      WRITE(6,7) (C(I),I=1,J)
      WRITE(6,8)
      WRITE(6,9) (I,X(I),Y(I),F(I),DIFF(I),PERER(I),I=1,N)
   11 CONTINUE

C EXPANSION OF FORSYTHE POLYNOMIAL
C

      L=M+1
      DO 19 I=1,L
      DO 19 J=1,L
      D(I,J)=0.0
      IF(I-J)19,35,19
   35 D(I,J)=1.0
   19 CONTINUE
      D(1,1)=0.0
      D(2,3)=-A(2)
      D(2,4)=A(2)*A(3)-B(2)
      D(3,4)=-(A(2)+A(3))
      D(2,5)=-A(2)*A(3)*A(4)+B(2)*A(4) +A(2)*B(3)
      D(3,5)=A(2)*A(3)+A(4)*A(2)+A(3)*A(4)-B(2)-B(3)
      D(4,5)=-(A(2)+A(3)+A(4))
      DO 20 J=6,L
      LL=J-1
      DO 20 I=2,LL
      D(I,J)=D(I-1,J-1)-A(J-1)*D(I,J-1)-B(J-2)*D(I,J-2)
   20 CONTINUE
      DO 22 J=1,M
```

SUBROUTINE FORS ...(CONT'D)

```
      S=0.0
      DO 21 I=1,M
      S=S+C(I)*D(J+1,I+1)
   21 CONTINUE
      C1(J)=S
   22 CONTINUE
      WRITE(6,40)
      WRITE(6,7)(C1(I),I=1,M)
      DO 341 I=1,N
      Z(I)=C1(1)+C1(2)*X(I)+C1(3)*X(I)**2+C1(4)*X(I)**3
     *+C1(5)*X(I)**4
      Z(I)=Z(I)*1185.0-460.0
  341 CONTINUE
      WRITE(6,373)(X(I),Y(I),Z(I),I=1,N)
  373 FORMAT(10X,3E18.6)
    1 FORMAT(I5)
    2 FORMAT(2E16.8)
    3 FORMAT(16H1AN EXPANSION OF,I4,2X,59HFORSYTHE
     * ORTHOGONAL POLYNOMIAL
    31S HAS A STANDARD DEVIATION OF,E17.8)
    4 FORMAT(30HJTHE FORSYTHE COEFFICIENTS ARE/38HJ   J
     *    A(J)
     1            B(J-1)//)
    5 FORMAT(1X,I2,2X,2E17.8)
    6 FORMAT(35HJTHE COEFFICIENTS C(1).....C(J) ARE)
    7 FORMAT(3X,6E17.8)
    8 FORMAT(6HK     I,7X,4HX(I),13X,4HY(I),13X,4HF(I),11X
     *,7HDIFF(I),6X,
     1 13HPERCENT ERROR//)
    9 FORMAT(1X,I4,5E17.8)
   40 FORMAT(32HJTHE POLYNOMIAL COEFFICIENTS ARE)
      RETURN
      END
```

SUBROUTINE SLOPE

```
      SUBROUTINE SLOPE(NE,NK,X,G,PAR1,II,TA,INR)
C
C        THIS SUBROUTINE CALCULATES THE VALUE OF THE
C        FUNCTIONS
C
      COMMON ISTEP,NPITOT,LRT
      COMMON A1(20),A2(20),A3(20),A4(20),A5(20),C6(20)
      COMMON YO2(20),YN2(20),YC4(20),CBT(20),COX(20)
      COMMON WG(20),PR(20),GG(20),NWT,NDS,TB,RR,WM,DRR
      DIMENSION X(20,8),G(10),PAR1(10),NPITOT(20)
      DOUBLE PRECISION PAR1
      XA=X(1,1)
      XB=X(1,2)
      XC=X(1,3)
      TG=X(1,4)
      A6=34.47
      A7=-.01998
      A8=34.07
      A9=10.0
      A10=34.68
      E1=PAR1(1)
      E2=-5.211
      E3=PAR1(2)
      E4=-9.66
      E5=PAR1(3)
      Q1=1.0E-04
      R1=1.0
      S1=0.0001
      T1=1.0
      U1=1.0E-04
      HR1=-75.0*1000.0
      HR2=60.0*1000.0
      HR3=70.0*1000.0
      HR4=-60.0*1000.0
      HR5=40.9*1000.0
      HR6=-15.5*1000.0
      HR7=-40.0*1000.0
      HF=2.8
      CAO=CBT(INR)
      CBO=COX(INR)
      WQ=WG(INR)
      GM=GG(INR)
   31 TQ=TG*TB
   14 TD=TA/10.0
      TW=A1(INR)+A2(INR)*TD+A3(INR)*TD**2+A4(INR)*TD**3
   12 DG=(WM*PR(INR))/(10.73*TQ)
      CPG=0.1903+1.8E-04*TQ-3.147E-08*TQ**2
      UG=0.04598+0.00004556*(TQ-660.0)
```

SUBROUTINE SLOPE ...(CONT'D)

```
      TKG=0.01762+0.0000233*(TQ-660.0)
      HW=0.027*(WQ*CPG)**.78*(TKG/DRR)**.22
      HW=HW*HF
      B2=DG/WQ
      F3=CPG*WM*GM
      F3=1.0/F3
      F3=F3/TB
   16 F1=(4.0*HW)/(DRR*CPG*WQ)
   36 EA=Q1*(EXP(A6-E1*RR/TG))
      EB=R1*(EXP(A7-E2*RR/TG))
      EC=S1*(EXP(A8-E3*RR/TG))
      ED=T1*(EXP(A9-E4*RR/TG))
      EE=U1*(EXP(A10-E5*RR/TG))
      C1=EA*(1.0-XA)*(1.0-XB)
      C3=EC*(1.0-XB)*XC
      C7=ED*(1.0-XA)
      C8=EE*CAO*(1.0-XA)
      C10=C1*CAO*CBO
      C11=C3*CAO*CBO
      EQ=1.0/EB
      DER1=C10+C7*CAO*(2.0*C10+C11)
      DER2=DER1+C10+C11
      DER3=DER1/(1.0+EB)-C11
      DER1=DER1+EE*CAO*(1.0-XA)
      PP=HR1*C10+HR4*C11+HR7*C8+(C10/(1.0+EQ))*(HR2+EQ*HR3)
     *+(2.0*C10+C11
     2)*((C7*CAO/(1.0+EQ))*(HR2+EQ*HR3)+HR5*C7*CAO+HR6)
      PP=PP*F3
      G(4)=PP-F1*(TG-TW)
      G(1)=DER1/CAO*B2
      G(2)=DER2/CBO*B2
      G(3)=DER3/CAO*B2
      RETURN
      END
```

```
$RUN  -LOAD#
08:52.03
   32.00000      28.00000      58.00000       0.42470   1185.00000
   4    3    3   20   20   10    4
   0.480000D 02      0.280000D 02      0.480000D 02
   0.100000D-01            1     0
  62
                  0.980907    -0.783087     3.145142    -2.562305
   0.122000E 02      0.537000E 02     0.115500E 04      0.741259E-01
   0.278856E 00      0.647018E 00
  0.0          0.0          0.0       695.00000
   5
   3     1     3     1     3
  2.54000     3.43000     4.31000     5.20000     6.10000
  40     20     20     20     20
   1     2     4
   0.01600     0.16000 672.00000
   4
 676.00000
   1     2     4
   0.03300     0.24600 705.00000
   4
 913.00000
   1     2     4
   0.12800     0.88800 970.00000
  63
                  0.976492    -0.714916     3.815235    -3.453647
   0.126000E 02     0.536000E 02      0.116200E 04      0.854260E-01
   0.321362E 00     0.593213E 00
  0.0          0.0          0.0       702.00000
   5
   3     1     3     1     3
  2.54000     3.43000     4.31000     5.20000     6.10000
  10     10     10     20     20
   1     2     4
   0.00750     0.09220 684.00000
   4
 696.00000
   1     2     4
   0.07190     0.38670 820.00000
   4
1041.00000
   1     2     4
   0.19190     0.946701032.00000
  64
                  0.982055    -0.943544     3.766500    -3.126618
   0.107000E 02     0.535800E 02      0.115200E 04      0.798990E-01
   0.300572E 00     0.619529E 00
  0.0          0.0          0.0       692.00000
   5
   3     1     3     1     3
  2.54000     3.43000     4.31000     5.20000     6.10000
  10     10     10     20     20
   1     2     4
   0.00340     0.11500 666.00000
   4
 670.00000
   1     2     4
   0.03740     0.21200 714.00000
```

```
    4
  825.00000
    1      2      4
    0.14800    0.935001025.00000
 THE TOTAL NO. OF DATA POINTS IS     33
```

```
    FOR TRIAL  0  DATA SET  1  WITH  11  POINTS
    THE INITIAL CONDITION IS

             0.0        0.0        0.0       694.9998
    THE CONSTANTS ARE
           0.4800D 02  0.2800D 02  0.4800D 02
      *     2.5400     0.1420     0.9479     0.0120   825.8323
      *     3.4300     0.1575     0.9935     0.0126   744.0569
      *     4.3100     0.1629     0.9987     0.0126   731.9275
      *     5.2000     0.1684     0.9997     0.0127   754.0413
      *     6.1000     0.1768     1.0000     0.0127   783.7324
    FOR TRIAL  0  DATA SET  2  WITH  11  POINTS
    THE INITIAL CONDITION IS

             0.0        0.0        0.0       701.9998
    THE CONSTANTS ARE
           0.4800D 02  0.2800D 02  0.4800D 02
      *     2.5400     0.1954     0.9738     0.0163   867.2234
      *     3.4300     0.2152     0.9979     0.0167   788.3411
      *     4.3100     0.2251     0.9997     0.0167   793.9182
      *     5.2000     0.2389     1.0000     0.0167   829.2295
      *     6.1000     0.2610     1.0000     0.0167   861.2881
    FOR TRIAL  0  DATA SET  3  WITH  11  POINTS
    THE INITIAL CONDITION IS

             0.0        0.0        0.0       691.9998
    THE CONSTANTS ARE
           0.4800D 02  0.2800D 02  0.4800D 02
      *     2.5400     0.1749     0.9859     0.0144   789.8713
      *     3.4300     0.1832     0.9981     0.0145   718.8108
      *     4.3100     0.1874     0.9996     0.0145   721.2251
      *     5.2000     0.1929     0.9999     0.0145   753.5271
      *     6.1000     0.2026     1.0000     0.0145   788.2585
    VARIANCE WITH INITIAL PARAMETER VALUES =     0.14120664D 00
          BEGIN STAGE  1
 PARAMETER VALUES AFTER ROTATION   1  ARE

              51.64      29.21      47.39
          BEGIN STAGE  2
    FOR TRIAL  1  DATA SET  1  WITH  11  POINTS
    THE INITIAL CONDITION IS

             0.0        0.0        0.0       694.9995
    THE CONSTANTS ARE
           0.5165D 02  0.2921D 02  0.4739D 02
      *     2.5400     0.0155     0.0670     0.0007   661.3496
      *     3.4300     0.0247     0.1246     0.0013   687.8989
      *     4.3100     0.0449     0.2539     0.0028   748.6179
      *     5.2000     0.1060     0.6039     0.0074   863.2603
      *     6.1000     0.1986     0.9361     0.0122   877.5842
    FOR TRIAL  1  DATA SET  2  WITH  11  POINTS
    THE INITIAL CONDITION IS

             0.0        0.0        0.0       701.9995
    THE CONSTANTS ARE
           0.5165D 02  0.2921D 02  0.4739D 02
      *     2.5400     0.0186     0.0670     0.0009   690.2244
      *     3.4300     0.0366     0.1553     0.0022   748.4155
      *     4.3100     0.1071     0.4828     0.0077   892.6655
```

```
        *     5.2000     0.2775     0.9499     0.0168   937.4548
        *     6.1000     0.3396     0.9942     0.0176   888.9609
     FOR TRIAL  1  DATA SET  3   WITH  11  POINTS
     THE INITIAL CONDITION IS

           0.0        0.0        0.0        691.9995
     THE CONSTANTS ARE
           0.5165D 02   0.2921D 02   0.4739D 02
        *     2.5400     0.0177     0.0744     0.0009   653.1692
        *     3.4300     0.0293     0.1437     0.0017   685.7280
        *     4.3100     0.0588     0.3196     0.0040   766.5051
        *     5.2000     0.1594     0.7933     0.0113   902.9426
        *     6.1000     0.2413     0.9786     0.0143   855.9133
          VARIANCE =          0.48362D-02
 PARAMETER VALUES AFTER ROTATION   2  ARE

             52.05       29.34       47.33
         BEGIN STAGE  3
     FOR TRIAL  1  DATA SET  1   WITH  11  POINTS
     THE INITIAL CONDITION IS

           0.0        0.0        0.0        694.9993
     THE CONSTANTS ARE
           0.5206D 02   0.2934D 02   0.4733D 02
        *     2.5400     0.0138     0.0514     0.0005   657.9277
        *     3.4300     0.0209     0.0927     0.0010   681.2859
        *     4.3100     0.0358     0.1818     0.0020   732.9546
        *     5.2000     0.0795     0.4336     0.0051   830.2747
        *     6.1000     0.1843     0.8686     0.0114   900.5774
     FOR TRIAL  1  DATA SET  2   WITH  11  POINTS
     THE INITIAL CONDITION IS

           0.0        0.0        0.0        701.9993
     THE CONSTANTS ARE
           0.5206D 02   0.2934D 02   0.4733D 02
        *     2.5400     0.0163     0.0510     0.0007   686.0559
        *     3.4300     0.0301     0.1130     0.0016   737.0479
        *     4.3100     0.0778     0.3301     0.0051   849.9036
        *     5.2000     0.2579     0.8917     0.0159   966.2771
        *     6.1000     0.3461     0.9886     0.0178   900.2563
     FOR TRIAL  1  DATA SET  3   WITH  11  POINTS
     THE INITIAL CONDITION IS

           0.0        0.0        0.0        691.9993
     THE CONSTANTS ARE
           0.5206D 02   0.2934D 02   0.4733D 02
        *     2.5400     0.0154     0.0562     0.0006   648.9614
        *     3.4300     0.0241     0.1046     0.0012   677.0015
        *     4.3100     0.0446     0.2216     0.0027   742.7549
        *     5.2000     0.1203     0.6042     0.0084   880.6290
        *     6.1000     0.2397     0.9554     0.0142   881.4866
          VARIANCE =          0.37058D-02
 PARAMETER VALUES AFTER ROTATION   3  ARE

             51.95       29.35       47.34
         BEGIN STAGE  4
     FOR TRIAL  1  DATA SET  1   WITH  11  POINTS
     THE INITIAL CONDITION IS

           0.0        0.0        0.0        694.9990
```

```
        THE  CONSTANTS  ARE
                0.5194D 02   0.2935D 02   0.4734D 02
          *     2.5400      0.0141      0.0542      0.0006   658.4771
          *     3.4300      0.0216      0.0977      0.0010   682.1990
          *     4.3100      0.0371      0.1915      0.0021   734.8035
          *     5.2000      0.0826      0.4539      0.0054   833.9961
          *     6.1000      0.1861      0.8776      0.0115   897.6887
        FOR  TRIAL   1   DATA  SET   2   WITH   11   POINTS
        THE  INITIAL  CONDITION  IS

                  0.0          0.0          0.0       701.9990
        THE  CONSTANTS  ARE
                0.5194D 02   0.2935D 02   0.4734D 02
          *     2.5400      0.0167      0.0538      0.0007   686.7078
          *     3.4300      0.0310      0.1191      0.0016   738.5239
          *     4.3100      0.0812      0.3480      0.0054   854.5527
          *     5.2000      0.2605      0.8998      0.0160   962.5815
          *     6.1000      0.3450      0.9891      0.0177   898.7952
        FOR  TRIAL   1   DATA  SET   3   WITH   11   POINTS
        THE  INITIAL  CONDITION  IS

                  0.0          0.0          0.0       691.9990
        THE  CONSTANTS  ARE
                0.5194D 02   0.2935D 02   0.4734D 02
          *     2.5400      0.0158      0.0593      0.0007   649.5994
          *     3.4300      0.0249      0.1103      0.0013   678.1211
          *     4.3100      0.0464      0.2335      0.0028   745.3091
          *     5.2000      0.1248      0.6277      0.0087   884.0779
          *     6.1000      0.2397      0.9580      0.0142   878.2036
              VARIANCE =         0.36441D-02
   PARAMETER  VALUES  AFTER  ROTATION    4    ARE

                   51.81        29.36        47.34
              BEGIN  STAGE   5
        FOR  TRIAL   1   DATA  SET   1   WITH   11   POINTS
        THE  INITIAL  CONDITION  IS

                  0.0          0.0          0.0       694.9988
        THE  CONSTANTS  ARE
                0.5180D 02   0.2936D 02   0.4734D 02
          *     2.5400      0.0145      0.0575      0.0006   659.1204
          *     3.4300      0.0223      0.1035      0.0011   683.2505
          *     4.3100      0.0385      0.2025      0.0022   736.8784
          *     5.2000      0.0859      0.4758      0.0057   837.7932
          *     6.1000      0.1877      0.8859      0.0116   894.4363
        FOR  TRIAL   1   DATA  SET   2   WITH   11   POINTS
        THE  INITIAL  CONDITION  IS

                  0.0          0.0          0.0       701.9988
        THE  CONSTANTS  ARE
                0.5180D 02   0.2936D 02   0.4734D 02
          *     2.5400      0.0172      0.0571      0.0008   687.4697
          *     3.4300      0.0322      0.1263      0.0017   740.2156
          *     4.3100      0.0850      0.3680      0.0057   859.6157
          *     5.2000      0.2628      0.9072      0.0161   958.5291
          *     6.1000      0.3437      0.9896      0.0177   897.3318
        FOR  TRIAL   1   DATA  SET   3   WITH   11   POINTS
        THE  INITIAL  CONDITION  IS

                  0.0          0.0          0.0       691.9989
```

```
THE CONSTANTS ARE
          0.5180D 02   0.2936D 02   0.4734D 02
  *       2.5400       0.0163       0.0629       0.0007    650.3433
  *       3.4300       0.0258       0.1169       0.0014    679.4031
  *       4.3100       0.0484       0.2470       0.0030    748.1467
  *       5.2000       0.1295       0.6517       0.0091    886.9753
  *       6.1000       0.2394       0.9603       0.0142    874.8674
     VARIANCE =               0.36231D-02
```