Feasibility Study for Producing Dimethyl Ether using Catalytic Distillation

by

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ABSTRACT

This research reports a feasibility study based on simulation for the production of dimethyl ether via the dehydration of methanol using catalytic distillation. Langmuir-Hinshelwood kinetic model is used for the reaction in the simulation. Simulations are based on a catalytic distillation column 2-inches (5.08 cm) in diameter. Parametric studies using Aspen Plus are used to determine the effect of parameters such as number of equilibrium stages, catalyst loading, catalyst location, reflux ratio, reboiler duty, feed rate, feed location, feed concentration, feed temperature and column pressure have on the concentration of catalytic distillation products and column temperature. It is found that the number of theoretical stages has no significant change on the product concentrations after 20 theoretical stages. Ten stripping stages are used to reduce methanol concentrations in the bottom, and the total number of theoretical stages is set to 30 for the base case, with condenser and reboiler as the first and last stage, respectively. Total catalyst loading is 2,800 grams of catalyst with 140 grams per stage and should be placed at the top of the column between stages 2 and 21 in a 30 stage column. It is determined that a reflux ratio of 4 is optimal for high dimethyl ether distillate concentrations. Reboiler duty should be kept at a minimum of 1.5 kW. Feed location of methanol is determined to be optimal directly above the catalyst bed regardless of catalyst location. Column temperatures are observed to be sensitive to changes in column pressure and feed rate. Column pressure has a positive correlation with distillate dimethyl ether concentration and column temperature.

DEDICATION

I would like to dedicate this work to my family. Their boundless love and support has allowed me to come this far. Without them I would not be the person I am today.

"Any sufficiently advanced technology is indistinguishable from magic"

- Arthur C. Clarke

ACKNOWLEDGEMENT

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ABBREVIATIONS

CD	Catalytic Distillation
CFCs	Chlorofluorocarbons
CI	Compression Ignition
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CSTR	Continuously Stirred Tank Reactor
DDMEFCs	Direct Dimethyl Ether Fuel Cells
DEFCs	Direct Ethanol Fuel Cells
DME	Di-methyl Ether
DMFCs	Direct Methanol Fuel Cells
DPF	Diesel Particulate Filters
EGR	Exhaust Gas Recirculation
ETBE	Ethyl Tert-Butyl Ether
GHG	Green House Gasses
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
MTBE	Methyl Tert-Butyl Ether
NO_X	Nitrous Oxides
PEMFCs	Proton Exchange Membrane Fuel Cells
PM	Particulate Mater
R-DWC	Reactive Dividing Wall Column
RR	Recycle ratio
SCR	Selective Catalytic Reduction
SO_X	Sulphur Oxides
Syngas	Synthesis Gas
TAME	Tert-Amyl Methyl Ether
ULEV	Ultra Low Emission Vehicle

Chapter 1

Introduction

Fossil fuels are currently the world's primary energy source, with oil being the main source for transportation (Courses, 2016). Burning of gasoline and diesel accounts for most of the transportation sector's greenhouse gas (GHG) emissions. Therefore, reduction in transportation emissions are essential in reducing overall emissions and climate change. Conventional fossil fuels are large producers of greenhouse gasses such as carbon dioxide (CO_2), nitrous oxides (NO_X), and sulphur oxides (SO_X), which are significant contributors to global warming. With the growth of the world's population, global demand for sustainable energy and fuel is on the rise. Fossil fuels, when burned are hazardous to the environment, thus the world is beginning to shift towards alternative forms of fuel and cleaner energy. An ideal fuel would have minimal environmental impact, be economical, safe, and provide high performance.

Di-Methyl Ether (DME), also known as methoxymethane, is a clean, colourless gas at room temperature with a mild odour. Due to DME's properties, it has significant potential not only as an automotive fuel or additive, but also for electric power generation, as an intermediate for chemical production, and domestic applications. DME can be made from methanol via synthesis gas which can be produced from a variety of sources such as biomass, residual oil, crude oil, coal, natural gas, forest products, agricultural by-products, fuel crops and municipal waste (Fang et al, 2011). With many different alternatives for feedstock there is much flexibility to produce DME, especially in places where oil is unavailable or difficult to attain. Many scientists and engineers are calling DME the "fuel of the future" for its attractive properties. Countries such as

China, Sweden, Korea, Egypt, Brazil, and Japan are already making the transition to DME as a key energy vector. Companies such as Oberon Fuels Inc., Akzo Nobel NV, DME Development Co., China Energy Ltd., Royal Dutch Shell, Korea Gas Corporation, Mitsubishi Corporation, Shenhua Ningxia Coal Industry Group Co., Grillo-Werke AG, Volvo Group, and Fuel DME Production Co., are a few companies who have already made significant investments towards DME (TMR Research, 2017). DME has a cetane number of 55-60, slightly higher than conventional diesel at 45-55 (Hosseininejad, 2010). Because DME does not contain any sulphur compounds it produces no sulphur oxides during combustion. It burns essentially soot-free and can produce lower amounts of nitrogen oxides by about 40% at higher exhaust gas recirculation compared to conventional diesel (Ying and Longbao, 2007). DME quickly decomposes into CO_2 and water in the atmosphere making it an environmentally friendly fuel (Lin, 2013). DME is easy to handle as it is non-toxic, non-corrosive, non-carcinogenic, non-mutagenic, and non-teratogenic (DuPont, 2012). DME has one of the highest well-to-wheel efficiencies with light and heavy-duty DME-fuelled vehicle efficiencies as 19% and 22.5%, respectively (Arcoumanis et al., 2008). As natural gas is one of the feed stocks that can be used to produce DME, many natural gas rich countries can benefit from DME's flexible production and distribution process. Oberon Fuels Inc. has made modular mini-plants that are transportable allowing for accessible DME production at the feed source (Oberon Fuels, 2018).

Similarly to liquefied petroleum gas (LPG), DME is gaseous at atmospheric pressure and temperature, but can be easily liquefied at moderate pressures above 0.5 MPa. Its similar chemical and physical properties to LPG allow for easy storage and transport using current LPG technology. LPG consumption can be reduced by using DME as a replacement or in equal

amount LPG-DME blends for domestic cooking and heating applications (Anggarani et al., 2014).

There are many methods used to make DME, with the conventional method being the conversion of synthesis gas (syngas) – a mixture of hydrogen and carbon monoxide gas, to methanol in a fixed bed reactor followed by purification and then dehydration of methanol to DME in another reactor. DME is then purified by separating unreacted methanol and water using a distillation column followed by another distillation column to separate water from methanol for recycling, which is quite energy intensive. Methanol production from synthesis gas is thermodynamically unfavorable, requiring high pressure for conversion. Methanol is becoming more abundant from other sources such as pulp and paper mills and municipal waste and more focus is being put on direct methanol dehydration to dimethyl ether, eliminating the need for a synthesis gas to methanol reactor and purifier (Hosseininejad, 2010).

One innovative method that shows much promise is the use of reactive or catalytic distillation (CD) to produce DME. Catalytic distillation is the integration of a chemical reactor and a distillation column into a single unit operation. With this new method, only one catalytic distillation unit is required for the full process, thus reducing the overall capital and utility costs. Catalytic distillation allows for constant separation of products from the reactants within the column, preventing the reaction from reaching equilibrium and creating better reactant conversion and a purer product. The heat of reaction will reduce the energy consumption of the single column, allowing for lower operating costs. Lastly, internal recycling of methanol will take place within the reboiler and condenser of the column.

The objective of this study was to conduct a parametric study using Aspen Plus simulation software to determine the optimal design parameters and operating strategies for the catalytic distillation process in the production of dimethyl ether from methanol.

Chapter 2

Background and Literature Review

Over the last century many different transportation fuels have been used, for example ethanol, methanol, fossil fuels, bio-diesel and bio-ethanol. Starting in the 1980's, DME has been used as an additive for ignition aid in diesel engines, also known as compression ignition (CI) engines. Later in 1988, pure DME was found to be a remarkable fuel for CI engines (Hosseininejad, 2010). To understand the benefits of DME it is important to have a thorough understanding of its properties, applications, and production.

2.1 Properties of DME

Hosseininejad (2010) gives a detailed comparison of DME's properties to other fuels as shown in Table 2.1. Dimethyl ether has a slightly higher cetane number than diesel. A higher cetane number lowers the fuel's ignition delay time and translates to quicker engine start, lower engine noise, improved fuel economy, increased engine power, and lower overall emissions (Green et al., 1997; Hashimoto, et al., 1996). The high oxygen content in DME (34.8 wt %) helps to reduce soot formation. One drawback to using DME is its lower heating value; approximately 1.3 times the mass or 1.5 times the volume of DME is required to meet the same heating value for diesel. DME is a colourless gas under atmospheric conditions (0.1 MPa and 298 K) and requires pressures above 0.5 MPa at 25 °C to be in the liquid phase (Arcoumanis et al, 2008). It is about one fiftieth the viscosity of diesel, leading to difficulties in engine lubrication and higher probability of leaks. Due to its mild odour and clear form as a gas, DME is difficult to detect

during leakage. To prevent leaks and increase odour, lubricating thickeners (Lubrizol or Hitec 560) and an odorant can easily be added. There has been much research for methanol as a fuel due to its high octane number of 100 and its reduced emissions of NO_X, SO_X, and PM. But methanol has its downfall for its low energy density, cold starting problems, and high metal corrosion (Hosseininejad, 2010). By blending methanol with DME many of its shortcomings can be avoided such as its cold starting issues, due to DME's very low boiling point of -24.9 °C at atmospheric pressure it has no issues of freezing or becoming too dense for flow.

Table 2-1: Properties of DME compared to other fuels

Property	Dimethyl Ether (DME)	Diethyl Ether (DEE)	Diesel	Methanol	Methane (LNG)	Propane/Butane (LPG)*
Chemical Formula	CH_3OCH_3	$C_2H_5OC_2H_5$	-	CH_3OH	CH_4	C_3H_8
Molecular weight (g/mol)	46.07	74.12	190-220	32.04	16.04	44.1
Oxygen content (mass %)	34.8	21.6	0	50	0	0
Density (kg/m^3) @ 15 °C	668	713	841	794	0.68	489
Viscosity (kg/m.s) @ 25 °C	0.12-0.15	0.224	5.35-6.28	0.768	-	-
Vapour pressure (bar) @ 25 °C	5.3	1.25	<0.1	0.31	NA	9.39
Critical pressure (atm)	52	36.7	29.7	81	45.96	41.94
Critical temperature (°C)	127	194	435	239	-83	97
Solubility in water (g/L) @ 20 °C	71	69	immiscible	miscible	0.035	0.062
Boiling point (°C) @ 1 atm	-24.9	34.5	180-350	64.8	-161.5	-42.1
Lower Heating Value (MJ/kg)	28.8		42.8	20.1	55.5	50.3
Cetane number	55-60	85-96	45-55	3	3	-
Autoignition temperature (°C)	235	170	210	460	538	450
Flammability limits in air (vol%)	3.4-27	1.9-36	0.6-6.5	5.5-36	5-15	2.2-9.6
Flash point (°C)	-41	-45	62	12	-188	-104

* (Rumble, 2017)

2.2 DME on Environment, Safety, and Health

Dimethyl Ether is very environmentally friendly compared to other transportation fuels, especially diesel. As a fuel, it produces little to no soot, particulate matter (PM), black smoke, or sulphur dioxides, and lower nitrous oxides emissions compared to diesel. When exposed to air, DME degrades by reacting to photo-chemically produced nitrate and hydroxyl radicals, having a half-life of 5.4 and 22 days, respectively. DME quickly reacts in the atmosphere to form water and carbon dioxide. If DME is spilled or exposed to soil, it will vaporize near the surface of the soil. However, DME has very high mobility in soil and can contaminate ground water (Howard, 1993). But a low boiling temperature and degradation by microorganisms makes ground water contamination a low concern (Olah et al., 2009). In water, DME does not adsorb to sediment or suspended PM, bioconcentrate in aquatic organisms, react with hydroxyls, or photolyze. If released into open water, it will volatize within 2.6 to 30 hours depending on the water flow and wind velocity (Howard, 1993).

DME is flammable and has low flammability limits (3.4 – 27 vol% in air), meaning that even at relatively low concentrations of DME, a flash or fire can occur in the presence of an ignition source. When ether is exposed to air, peroxides can be formed which are very explosive. For dimethyl ether at normal conditions, peroxide formation is minimal compared to other ethers and a free radical inhibitor can be used to prevent any peroxides from being produced (Basu et al., 2001). As DME is usually stored in pressurized vessels and is flammable, extreme caution should be taken in handling or storing DME to prevent any explosions. Containers and vessels should be fit with appropriate pressure relief valves designed to vent contents when exposed to elevated temperatures or pressures (Praxair, 2016).

DME is non-toxic, non-carcinogenic, and non-mutagenic. The main exposure of DME to the human body occurs by inhalation. Effects of single overexposure to DME by inhalation may cause incoordination, headaches, blurred vision, analgesia, unconsciousness and cardiac irregularities (Praxair, 2016). DME has very low reactivity in humans and has no irreversible damage to health in both short and long-term periods.

2.3 Applications of DME

DME has received considerable praise for its potential as a multipurpose fuel. It is considered as a non-petroleum based clean and high-performance compression ignition fuel (Arcoumanis et al., 2008). DME is also used as a refrigerant, extraction and solvent agent, catalyst and stabilizer for polymerization, and as a propellant for sprays (Howard, 1993).

DME is an attractive substitute for gasoline, diesel, and liquefied petroleum gas (LPG). There are many advantages to using DME as fuel. With the chemical formula of CH_3-O-CH_3, its absence of C-C (Carbon-Carbon) bonds and its very high oxygen content of 34.8 wt % eliminates production of soot, particulate matter, or black smoke (Singh, 2008: Arcoumanis et al., 2008). The elimination of soot or particulate matter has tremendous benefits to automobile diesel engines. It allows for higher exhaust gas recirculation (EGR) – recycling of engine exhaust containing combustion inert gases to lower combustion chamber temperatures – in diesel vehicles. This leads to lower nitrous oxides (NO_X) emissions because increased amounts of NO_X is formed at high temperatures in the presence of oxygen and nitrogen. Increasing EGR will normally increase PM in a vehicle's exhaust but since DME produces little to no PM there are little to no visible repercussions for increasing EGR. With high EGR, low enough NO_X

emissions could allow for the elimination of selective catalytic reduction (SCR) catalysts and an ammonia injection system or can be used in conjunction with high EGR to reduce NO_X emissions significantly to ultra low emission vehicle (ULEV) limits. In diesel engines, the need for very expensive diesel particulate filters (DPF) would also no longer be required, in turn removing the filter regeneration process of increased fuel injection to burn off accumulated filter soot at high temperatures (~600 °C). No soot also means less engine oil contamination which leads to less abrasion and wear and longer engine life. DME can be used in diesel engines with proper sealing to the engine and fuel tank, and some modifications to the fuel injection (Arcoumanis et al, 2008). DME vehicles have already been developed and tested around the world in countries such as China, Sweden, and Japan. The Swedish company Volvo Trucks has partnered with Oberon Fuels Inc. to help produce and supply trucks and busses fueled by DME. In 2008, China initiated a demo fleet of 10 DME buses with its first DME refill station. The buses have shown much promise with reduced CO, hydrocarbons, NO_X, PM, and smoke. They have also shown an improved fuel economy of about 5% compared to diesel and gasoline-powered buses (Fleish et al, 2012).

The most common form of international trade is done through ships. Marine fuel is one of the highest sulphur content fuels (2-4 wt% sulphur) used for transportation. There are thousands of ships in the world transporting goods burning nearly 4-7 million barrels of high sulphur bunker fuel a day. Each ship is equivalent to having nearly 500 more cars on the road per annum (Endresen et al., 2006; Evans, 2009). With new International Maritime Organization (IMO) regulations all marine fuel will be required to contain less than 0.50 wt% sulphur and PM by the start of 2020 (International Maritime Organization, 2016). With stricter regulations approaching

fast and significant pollutions from ships, there is even further demand for high quality diesel such as sulphur free DME.

Many power stations generate electricity through steam turbines that use heat energy produced from burning coal, petroleum, or natural gas. When coal is burned, it produces much more CO_2 than conventional hydrocarbons and contains considerable amounts of sulphur that require expensive units to extract. In Japan, JFE Engineering, Iwatani International Corp. and Daihatsu Diesel have joined to construct the world's largest DME power generation facility with a capacity to produce 1250 kW of energy. After some design alterations of diesel power generating engines, the demonstration plant showed a higher efficiency, lower costs, and one-tenth of diesel NO_X emissions (Shimizu et al. 2009). DME-fuelled gas turbines have shown a comparable power generation efficiency of 1.6 - 2.8 % higher than natural gas, and 6 – 7 % than liquid naphtha. With thermochemical recuperation, the increase in power output can be as high as 44 % with an 8 % decrease in CO_2 emissions (Cocco et al., 2006).

DME produces a bright blue flame when ignited and can be used as a substitute for liquefied petroleum gas. Household heating and cooking is largely done using LPG or natural gas, especially in Japan, Indonesia, and China which are heavily reliant on LPG for domestic use. Studies by Anggarani et al (2014) show that LPG can be blended with DME of up to 50 % with only a slight decrease in thermal and fuel efficiency when used in conventional LPG stoves.

DME is also extensively used as an aerosol propellant replacing previously environmentally harmful chloro-fluoro-carbons (CFCs). DME plays a significant role in the cosmetic, beauty, and health industry. Majority of air fresheners, hair sprays, antiperspirants, deodorants, and pain relieving sprays use DME as an aerosol propellant.

Low temperature working fuel cells such as proton exchange membrane fuel cells (PEMFCs), direct ethanol fuel cells (DEFCs), and direct methanol fuel cells (DMFCs) are widely explored. Due to their limitations in either fuel storage, toxicity, safety, or reactivity more research is being conducted towards DME for fuel cells. The advantages to using DME fuel for fuel cells are: easier oxidation of DME into CO_2 due to no C-C bonds, decrease in anode-cathode cross-over because of low DME dipole momentum, low toxicity and flammability, and lastly its relatively high explosive limit. Despite direct dimethyl ether fuel cells (DDMEFCs) having a lower electrical performance than DMFCs, further catalyst optimization and research could lead to higher fuel cell efficiency in the future (Kerangueven et al., 2005). DME can also be used as an intermediate for production of light olefins, methyl acetate, propylene, gasoline, hydrogen, acetic acid, and dimethyl sulphate.

2.4 DME Production

DME is mainly produced through the dehydration of methanol (Equation 2.3). Conventionally, methanol is produced from synthesis gas or as a by-product of industrial processes, such as in the pulp and paper industry.

There are many different raw materials that can be used to make DME. Any source that can produce synthesis gas can be used to make DME. As shown in Figure 2.1, many forms of biomass, a renewable material can be used as feed for synthesis gas and in turn for DME (Hosseininejad, 2010).
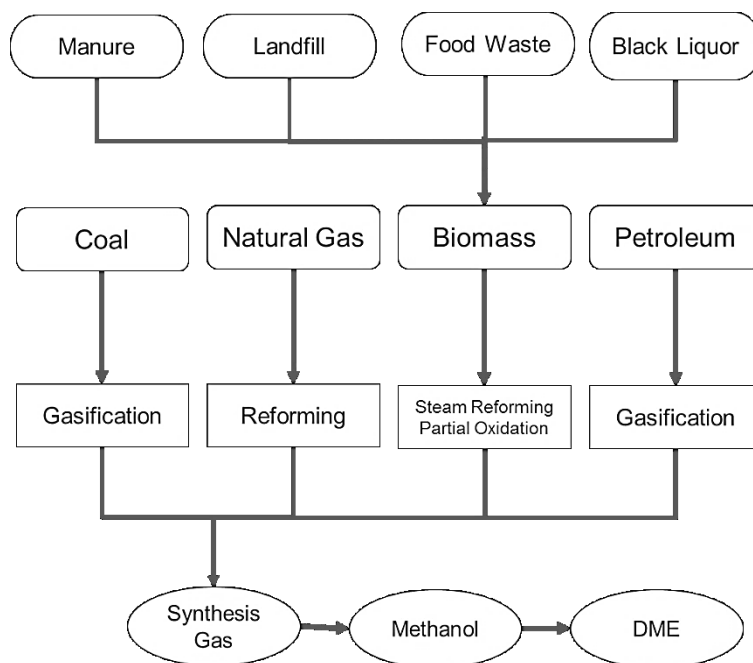
Figure 2.1: Sources for DME Production

2.4.1 Direct Synthesis

In the direct synthesis processes described by Peng et al., (1997), synthesis gas can be directly converted into DME in a single step process over bi-functional catalyst. Taking advantage of the fact that the methanol synthesis and dehydration reaction occur at similar conditions, both reactions can be completed in a single slurry phase bubble-column reactor or a continously stirred tank reactor (CSTR). The slurry phase bubble reactor keeps the exothermal reaction at a constant temperature while maximizing catalyst performance. As decribed in the article by Peng et.al., (1997), the three reactions (Equations 2.1-2.3) that take place in the reactor form a synergistic system. The methanol dehydration reaction (2.3) drives the synthesis reaction (2.1) forward away from equilibrium. While water pushes the dehydration reaction backwards and is produced in reaction (2.3), it is consumed by the water gas shift reaction (2.2). The hydrogen

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then formed by the gas shift reaction (2.2) increases the rate of methanol synthesis, allowing for continous forward reactions to occur simultaneously. Synergy of the reactions occurs best with carbon moxide rich synthesis gas (Peng et.al, 1997).

Methanol synthesis: $\qquad CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298K} = -90.8 \text{ kJ mol}^{-1}$ (2.1)

Water gas shift reaction: $\qquad CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -49.8 \text{ kJ mol}^{-1}$ (2.2)

Methanol dehydration: $\qquad 2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad \Delta H_{298K} = 41.0 \text{ kJ mol}^{-1}$ (2.3)
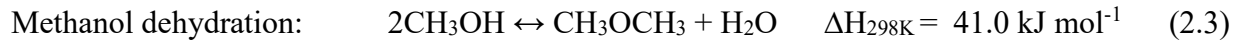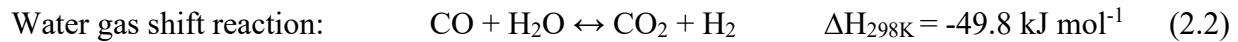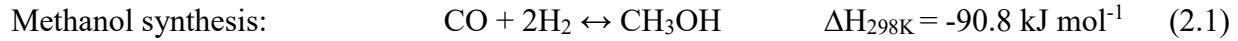
As mentioned previously, methanol is becoming more abundant from sources other than syngas making this process less attractive. Also, the catalyst interaction for methanol synthesis and methanol dehydration causes both catalysts to deactivate rapidly possibly due to inter-catalyst mass transfer (Peng et al., 1997)

2.4.2 Indirect Synthesis

In this two-step process both methanol and DME are produced in separate fixed-bed reactors. In general, syngas is used to produce methanol over a copper-based catalyst, the methanol is then sent into another reactor using γ-alumina or zeolite catalyst for DME production by dehydration. In conventional methanol dehydration reactors, the reaction takes place at 250-400 °C and a pressure of up to 20 bar (Kiss and Suszwalak, 2012). After reaction, the DME is then purified using at least two distillation columns to remove unreacted methanol and any water (Hosseininejad, 2010). Thus, the indirect method tends to be a very energy intensive and an expensive process.

2.4.3 Membrane Reactor

Water acts as an inhibitor to DME production as it competes with methanol for active catalyst sites and shifts the equilibrium reaction towards the reactants. Sea and Lee (2006) used an alumina-silica membrane reactor to remove water during the methanol dehydration reaction. The alumina-silica membrane allowed for water vapour to permeate out of the system while keeping methanol and dimethyl ether in place. It is important to keep in mind that water permeable membranes require high water permeation to separate the water as quick as it forms in the reaction. Their study showed that nearly 15% more conversion of methanol takes place with the use of alumina-silica membrane reactors (Sea and Lee, 2006).

2.5 Catalytic Distillation

The concept of reactive distillation in chemical processing was first cited in the 1960's (Sundmacher and Kienle, 2006). One of the earliest example was by DuPont in which dimethyl terephthalate was reacted with ethylene glycol in a column to produce and separate methanol and ethylene terephthalate for polyester production. Academic research and corresponding literature on catalytic distillation was scarce until 1970. Reactive distillation was not popular until about three decades ago. The publication by engineers from Eastman Chemical Co. sparked interest on catalytic distillation in both academia and industry. The process utilized a catalytic distillation column to produce methyl acetate from the top and water from the bottom. The reactant methanol is fed near the lower part of the column while acetic acid from the upper part. This process of a single catalytic distillation unit replaces a complex conventional flowsheet of 11 process units. With this technology both capital and energy costs were reduced by a factor of five

(Yu and William, 2009). Reactive distillation is also popular for its use in the production of methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amyl methyl ether (TAME). Catalytic distillation has successfully been applied in commercial applications for hydrogenation, isomerization, etherification, hydrodesulphurization, and oligomerization reactions. It also has significant potential for reactions such alkylation, acetalization, hydrolysis, hydration, dehydration, and transesterification.

One of the greatest features of catalytic distillation is the simultaneous production and separation of products in a single unit operation. In reversible chemical reactions, the continuous removal of product components drives the reaction towards the product side leading to high chemical conversions (Gates and Johanson, 1971). By using catalytic distillation, higher selectivity can be achieved, reaction equilibrium limitations can be overcome, undesirable side reactions can be avoided, heat of reaction can be directly used for distillation, and closely boiling mixtures or azeotropes can be more easily separated than by using conventional unit operations (Sundmacher and Kienle, 2006). A good example of using catalytic distillation to prevent side reactions is the process for producing ethylene glycol. Conventionally, ethylene glycol is produced by direct dehydration of ethylene oxide. Side reactions with glycol and ethylene oxide take place to form di-ethylene glycol, tri-methylene glycol, and tetra-ethylene glycol. This leads to the use of three evaporators and a distillation column to remove side products, but with catalytic distillation no side products are formed as ethylene glycol is extracted before it forms significant amounts of di-ethylene glycol. From there the side reactions are prevented and high purity ethylene glycol is produced in a single unit (Samoilov et al., 2006). Despite the many advantages of catalytic distillation, it is limited by its need for matching temperatures that provide favorable reaction rate and favourable separation. Since both distillation and reaction occur in a single unit, the

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dynamic and steady-state operation of reactive distillation can be very complex. If the reaction rate occurs faster than product separation, the product concentration will drive the reaction equilibrium back towards the reactants. If the reaction rate is slower than product separation, then product contamination with reactants during separation is very likely.

Presently, there has been little experimental research conducted to produce Di-Methyl Ether (DME) using catalytic distillation. Significant research in the field of DME synthesis using catalytic distillation is primarily on simulation modelling. Simulations by An et al., (2004) showed that a 30-stage single catalytic distillation column for DME production could offer significant economic advantages to produce high purity DME. Amberlyst 35 was the catalyst of choice in their simulations. Their simulation operating conditions are shown in Table 2.2.

Table 2-2: Simulation input parameters for catalytic distillation of methanol to DME

Feed Stream		CD Column	
Temperature:	298 K	Total Stages:	30
Pressure:	0.9 MPa	Rectification Stages:	1-7
Flow Rate:	2.5 mol/s	Reaction Stages:	8-20
Feed Composition:	MeOH	Stripping Stages:	21-30
		Feed Stage:	8
		Catalyst Loading:	9.23 kg/stage
		Column Pressure:	0.9 MPa
		Reflux Ratio:	9
		Distillate to Feed Ratio:	0.5

Their simulation results demonstrated that approximately 99.99 mol % DME can be obtained from the distillate and nearly pure water from the bottom stream. They also investigated the effects of total number of equilibrium stages, feed stage, reaction zone, column pressure, and reflux ratio have on the distillate DME concentration. From their analysis, they determined that increasing the total number of stages improved the purity of DME and water products up to 30 stages, and then no further significant improvements in purity were observed. Their simulations showed that placing the feed stage near the top of the reaction zone within three stages from the first catalyst stage, maximized the reaction rate and minimized methanol entrainment in the distillate. The catalyst amount for the reaction zone was determined by an optimum value considering the reflux ratio. Results showed that column pressure was found to affect reaction rates significantly by influencing the column temperature profiles. It was determined that decreasing the column pressure would decrease the temperature profiles and hence lower reaction rates and purity in the product streams. They indicated that increasing the reflux ratio positively influences both separation and reaction rate in catalytic distillation. Therefore, they claim by increasing the reflux ratio, the rate increases the reactant methanol recycle rate and its concentration across the reaction zone leading to higher conversion to DME.

An innovative method proposed by Kiss and Suszwalak (2012) contained a dividing wall in a reactive distillation for DME synthesis which could significantly increase energy savings between 12-58 %, reduce CO_2 emissions by 60 %, and lower capital costs by 30 %. A dividing wall column splits the middle of a column into two sections by inserting a vertical wall in the tower, allowing for the reaction to occur in one section and significant separation in the other. Using sequential quadratic programming (SQP) to produce 99.99 wt % DME at a constant feed rate, three process alternatives were simulated and compared: conventional process, reactive

distillation, and reactive dividing wall column (R-DWC). The results showed that R-DWC has not only the lowest energy requirements per ton of DME but also the lowest investment costs of the three processes. In the research the SQP method optimizes column configurations such as total number of stages, reactive stages, location of reactive zone, location of feed, length of dividing-wall, reflux ratio, and boilup rate to produce 99.99 wt % DME in the distillate at a constant feed while keeping overall heat duty at a minimum. Kiss and Suszwalak (2012) also stated that simply having a reactive distillation is not sufficient as significant methanol contamination is present in the bottom water stream and a secondary distillation column is needed for separating and recycling methanol from water. Hence, the operational and capital costs of the reactive distillation process alternative would be greater than the conventional process. Contradictory to other research which state that appropriate optimization of a reactive distillation can eliminate methanol contamination in both distillate and bottom products at >99.9 wt % DME production, thus eliminating the need for a secondary distillation column (An et al., 2004; Lin, 2013; Su et al., 2016). The reaction kinetics for all the process alternatives was represented by Eley-Rideal reaction kinetics but was input into the SQP program as a modified power-rate law for programming simplicity (Kiss and Suszwalak, 2012).

An improved process was proposed by Lei et al., (2011), consisting of a fixed bed reactor followed by a catalytic distillation column. They simulated and compared the conventional and reactive distillation processes. Their results showed that implementing a fixed bed reactor before catalytic distillation can reduce reboiler and condenser duty by 26.22 % and 26.85 %, respectively, compared to the conventional process. In comparison to the catalytic distillation with a secondary distillation column, their method will reduce total reboiler and condenser duty by 87.66 % and 84.06 %, respectively, and increase total methanol conversion by 50 %. With the

addition of a fixed bed reactor the catalytic distillation stages can also be reduced from 30 stages to 15. Since the conventional process already utilizes a fixed bed reactor and two similar sized distillation towers the implementation of their method would only require addition of catalyst in one of the distillation columns in the traditional method (Lei et al, 2011). Unfortunately, the research did not compare the process with a single optimized catalytic distillation column.

Su et al. (2016) proposed the use of a dual-catalyst system. Amberlyst 35 is the catalyst of choice for most DME catalytic distillation processes due to its high conversion rate at low temperatures in the range of 110-135 °C. To operate catalytic distillation below temperature limits for Amberlyst 35 the column pressure is suggested to be optimal at 900 kPa. They stated that further increases in pressure will increase separation and temperature profiles, which in turn increases reaction rates, but also causes temperature profiles to exceed catalyst temperature limitations (>150 °C). Su et al. (2016) experimented with the addition of Amberlyst 70 to higher temperature sections of catalytic distillation. Amberlyst 70 is a solid-acid catalyst like Amberlyst 35 but with-more stability, less conversion, and a maximum operation temperature of 190 °C. Despite the decrease of DME concentration in the distillate DME and bottom water concentrations from 97.2 wt % to 92.3 wt % and 93.2 wt % to 82.5 wt %, respectively, the use of dual-catalyst systems offers some advantages. Su et al. (2016) found that Amberlyst 35 activity decreases at a faster rate at temperatures exceeding 130 °C and that replacing the bottom stages of the column exceeding 130 °C with Amberlyst 70 slowed down the total catalyst deactivation time and allowed for higher temperature profile operations. Dual-catalyst systems allowed for higher pressures within the column due to increased temperature limitations, with the addition of Amberlyst 70. A higher column pressure of 11 bar increases the dew point of DME to 48.3 °C allowing for industrial grade cooling water at 33 °C to be used in the condenser (Su et al., 2016).

Despite the decrease in catalyst deactivation time and cooling water supply, the increase in column temperature and pressure will add to utility costs.

The next chapter discusses the details for optimizing a catalytic distillation by determining the optimal parameters of number of equilibrium stages, catalyst loading, reflux ratio, reboiler duty, feed rate, and column pressure for high purity DME production.

Chapter 3

Simulation Results

3.1 Introduction and Overview

The chemical process simulation program Aspen Plus® V8.8 by AspenTech was used to simulate the catalytic distillation column. The rigorous equilibrium stage unit RADFRAC is the only unit in Aspen Plus that can model combined distillation and reaction, and was used for this reason. The reaction type was entered as REAC-DIST which uses either a built-in power law or a user subroutine to calculate reaction rates for all components at each stage of the reaction zone. Since the dehydration of methanol to dimethyl ether is not well represented by a power law kinetic model, a user subroutine was used. The subroutine was developed using Fortran (Appendix C) and compiled using Microsoft Visual Studio 2013. The NRTL (Non-Random Two Liquid) thermodynamic model was used because methanol, water, and DME are polar with different molecular sizes leading to particle distribution as non-random, due to intermolecular forces and hydrogen bonding dominating between molecules. As seen in Table 3.1, polar liquids that are a mixture of water and organics or dissimilar organics (ethers-alcohols) are best represented by NRTL, Wilson, UNIFAC, or UNIQUAC thermodynamic models (Justice, 2011). Since Aspen Plus has an extensive database of binary interaction parameters (BIPs) and the system is comprised of a mixture of polar liquids that can be assumed as non-random, therefore NRTL is an excellent model for our system.

Table 3-1: Most commonly used thermodynamic models

Model Category	Most Commonly Used Models	System Type	Examples
Equation of State (EOS)	SRK Peng-Robinson	Real Gas + Ideal Liquid	Petroleum pseudo-components Similar hydrocarbons Light gasses
Binary Interaction Parameter (BIP) Activity Coefficient	NRTL Wilson	Ideal Gas + Polar Liquid	Water + Organics Dissimilar hydrocarbons (e.g., benzene-cyclohexane)
Predictive Activity	UNIFAC UNIQUAC		Mineral acids + water Dissimilar organics (e.g., esters-alcohols)
Electrolyte	NRTL	Aqueous Electrolyte	Water + Acid, base or salts

It was assumed that there was no pressure drop across the column. The operating pressure of the column was specified in the first instance at 900 kPa to ensure that the methanol for the reaction was in the liquid phase. The simulations were conducted for a 2 inches (5.08 cm) internal diameter column.

3.2 Catalyst

To design or model any reactive process, reaction kinetics must first be determined. Solid-acid catalysts are commonly used for the dehydration of methanol to DME. There are a variety of solid-acid catalysts such as zeolites, γ-alumina, ion exchange resins, and metal oxides. These catalysts can be modified with different compositions to improve activity, strength or performance for the dehydration of methanol. Ion exchange resins are preferred over other solid-acid catalysts because of their high selectivity for DME and relatively low operating temperature

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(30–150 °C) which is favoured for simultaneous DME-methanol-water separation (Spivey, 1991). Some examples of ion exchange resins used for catalytic dehydration of methanol are Amberlyst 15, 35, 36, and 70. Amberlyst 35 and 36 have higher DME production and initial rate of reaction at lower reaction temperatures and at higher initial water concentrations than Amberlyst 15 and 70 (Hosseininejad et al., 2012). Amberlyst 15 also has less tolerance to elevated temperatures at which higher conversion can be achieved (An et al., 2004). Amberlyst 35 was preferred over Amberlyst 36 because of its better catalytic properties, increased physical stability, and less swelling than Amberlyst 36 (Hosseininejad et al., 2012). Many researchers have postulated that Amberlyst 35 follows either Langmuir-Hinshelwood (Gates and Johanson, 1971; Hosseininejad et al, 2012) or Eley-Rideal (An et al, 2004; Kiviranta-Pääkkönen et al., 1998) reaction mechanism. The difference between the model kinetics is the molecular adsorption on the catalyst acid sites. In the Eley-Rideal model only one molecule adsorbs on the acid site and then reacts with a second molecule from the liquid bulk phase. In the Langmuir-Hinshelwood model two molecules adsorb onto adjacent acid sites and then react. In both kinetic models, water is an inhibitor to the production of DME as it competes with methanol to occupy acid sites. For the dehydration of methanol to DME a generic rate expression was given as:

$$r_{DME} = \frac{k_S K_M^2 C_M^2}{(1 + K_M C_M + (K_W C_W)^n + K_D C_D)^m} \tag{3.1}$$

k_S is the surface reaction rate constant and C_M, C_W, C_D, K_M, K_W, and K_D are the concentrations and adsorption equilibrium constants for methanol, water, and DME respectively. The value of n is 0.5, 1, or 2. When the power m is 1 the equation is the Eley-Rideal model and when m is 2 it is a Langmuir-Hinshelwood model.

Hosseininejad et al., (2012) experimented with catalytic dehydration of methanol over several catalysts in an autoclave reactor over the temperature range of 110 – 135 °C at a pressure of 0.9 MPa. They found that Amberlyst 35 not only gave the best results for methanol dehydration at low temperatures and pressure but also that the experimental results were well represented using the Langmuir-Hinshelwood model. Considering many factors, including the low adsorption of DME compared to water and methanol. They proposed the following rate equation for the dehydration of methanol to DME using Amberlyst 35:

$$r_{DME} = \frac{k_S \, C_M^2}{\left(C_M + \frac{K_W}{K_M} C_W \right)^2}$$

(3.2)

K_W/K_M is the ratio of the adsorption equilibrium constants of water and methanol, denoted by

$$\frac{K_W}{K_M} = \exp\left(-6.46 + \frac{2964}{T}\right)$$

(3.3)

T is the temperature in Kelvin. The surface reaction rate constant k_S in Equation (3.2) was reported by Hosseininejad et al. (2012) as:

$$k_S = 6.12 \times 10^7 \, \exp\left(-\frac{11{,}787}{T}\right) \frac{\text{kmol}}{\text{kg}_{\text{cat}} \cdot \text{s}}$$

(3.4)

T is the temperature in Kelvin.

3.3 Preliminary Studies

Preliminary simulations were carried out to identify base case operating parameters for a catalytic distillation column having a 5.08 cm inner diameter. Simulations showed that a reflux ratio of 4, a reboiler duty of 1.5 kW and a feed rate of pure methanol at 100 mol/h with a column pressure of 900 kPa gave a reasonable vapour-liquid traffic in the column. Using these starting values, the next step was to determine the catalyst mass and number of equilibrium stages required to achieve the desired performance. The target performance criteria were to maximize DME concentration in the condenser and minimize the methanol concentration in the reboiler. The latter constraint is especially important, because it is very energy intensive and expensive to separate water and methanol in a subsequent distillation column.

The amount of catalyst loaded onto each stage in the reaction zone is a key parameter, which will affect the reaction rate. With higher catalyst loading, one would expect a higher conversion rate for methanol to DME. The optimum amount of catalyst should be determined in conjunctions with feed rate to the column. In all simulation, the feed rate of pure methanol to the column was kept constant at 100 mol/h. The first set of simulations was conducted by varying the total catalyst mass over the range from 1.0 to 4.5 kg, which was distributed uniformly amongst the column stages. The number of catalytic stages was varied from 5 to 50. The stages were numbered from the top to the bottom, with stage 1 as the condenser and the last stage as the reboiler. Figures 3.1(a) and (b) show the mole fractions of DME and methanol variation as a function of the number of catalytic stages for various catalyst loadings.
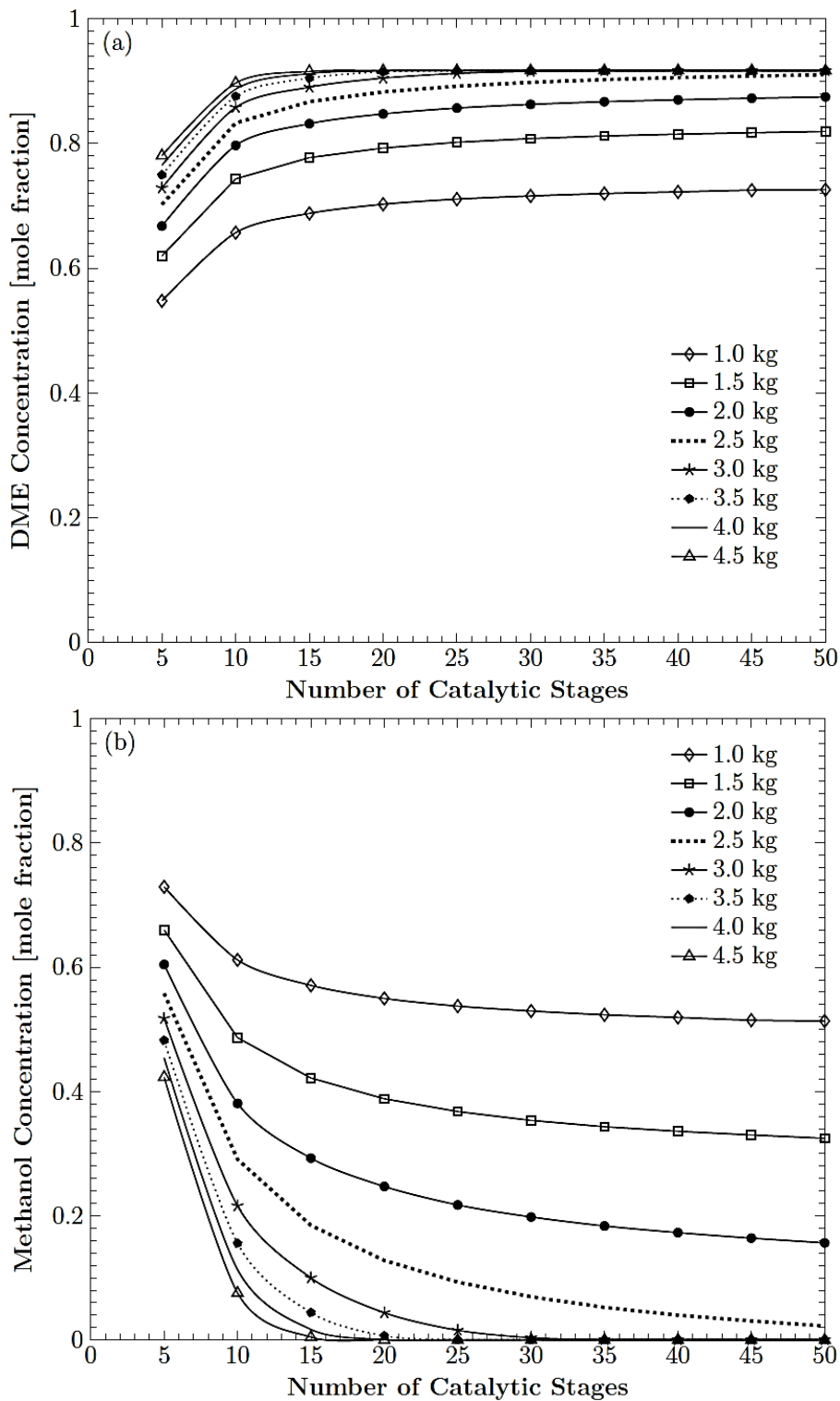
Figure 3.1: Effect of total catalyst mass on distillate DME (a) and bottom methanol (b) concentrations for reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa column pressure

Both figures show that the DME mole fraction in the overhead increases with an increase in catalyst mass, and that the methanol mole fraction in the bottom product stream decreases. For all catalyst masses, the DME and methanol concentrations do not change significantly after about 20 stages. Both figures also show that, to achieve greater than 90 mol % DME in the overhead and negligible methanol concentration in the bottom product, requires at least 3.5 kg of catalyst.

The manufacture specification sheet for Amberlyst 35 indicates that the maximum allowable temperature is 150 °C, above which temperature the catalyst will rapidly lose activity and selectivity. If the temperature in the reaction zone is too high, it will cause the catalyst to deactivate leading to reduction of conversion rate and lose efficiency for the catalytic distillation column. At too low a temperature the catalyst will not provide enough driving force for the reaction and will reduce the reaction rate. Therefore, it is important to consider the liquid-phase temperature profile. Figure 3.2 shows the simulation results of the liquid-phase temperature profile in the column having a 20- stage reaction zone containing 3.5 kg of evenly distributed catalyst. The simulation results show that the liquid-phase temperature increases more than 150 °C between stages 19 and 21 of the reaction zone. This will cause the catalyst to deactivate leading to lower conversion rate. Because the reaction is exothermic, reducing the total amount catalyst loading on each stage in the reaction zone could lead to lower the liquid-phase temperature in the reaction zone.
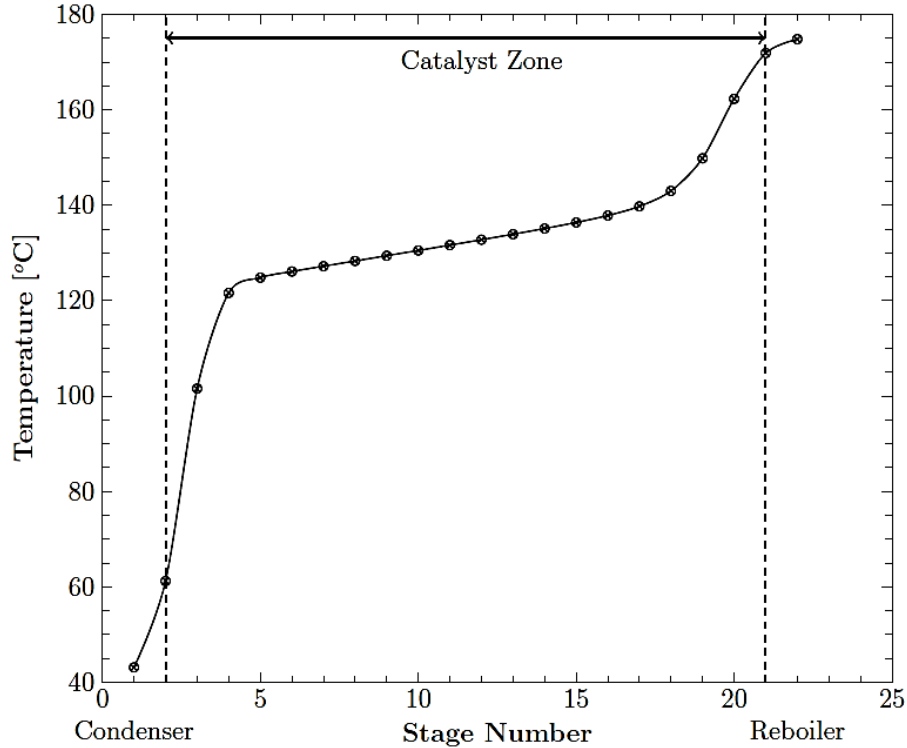
Figure 3.2: Temperature profile across reactive distillation column for total catalyst loading of 3.5 kg between stages 2 and 22 at reflux ratio of 4, reboiler duty of 1.5 kW, and feed rate of 100 mol/h at 900 kPa

Figure 3.3 shows the temperature profiles in the column for various catalyst loadings on each stage in the reaction zone at a reflux ratio of 4, reboiler duty of 1.5 kW, and feed rate of 100 mol/h at 900 kPa. It is evident that as the catalyst loading decreases the temperature profile in the catalyst zone. For catalyst loadings below 3.0 kg have a temperature profile of less than 150 °C within the catalyst loading zone. As seen in Figure 3.1(a), to achieve greater than 90 mol % DME in the overhead more than 2.5 kg of catalyst is required. It can be concluded that the catalyst loading must be between 2.5 and 3.0 kg to meet the target performance of more than 90 mol % overhead DME and less than 150 °C temperature within the reaction zone. Through trial simulations it was determined that 2.8 kg of catalyst had the highest concentration of DME in the

distillate at 90.1 mole % without exceeding a temperature of 150 °C within the catalyst zone. However, Figure 3.1(b) shows that the methanol concentration in the bottom product stream is significant for catalyst loading between 2.5 and 3.0 kg. To reduce the methanol concentration in the bottom stream without increasing the catalyst loading and the liquid-phase temperature in the reaction zone, stripping sections were added. Their effect on bottom concentration was examined at a reflux ratio of 4, reboiler duty of 1.5 kW, and feed rate of 100 mol/h at 900 kPa.
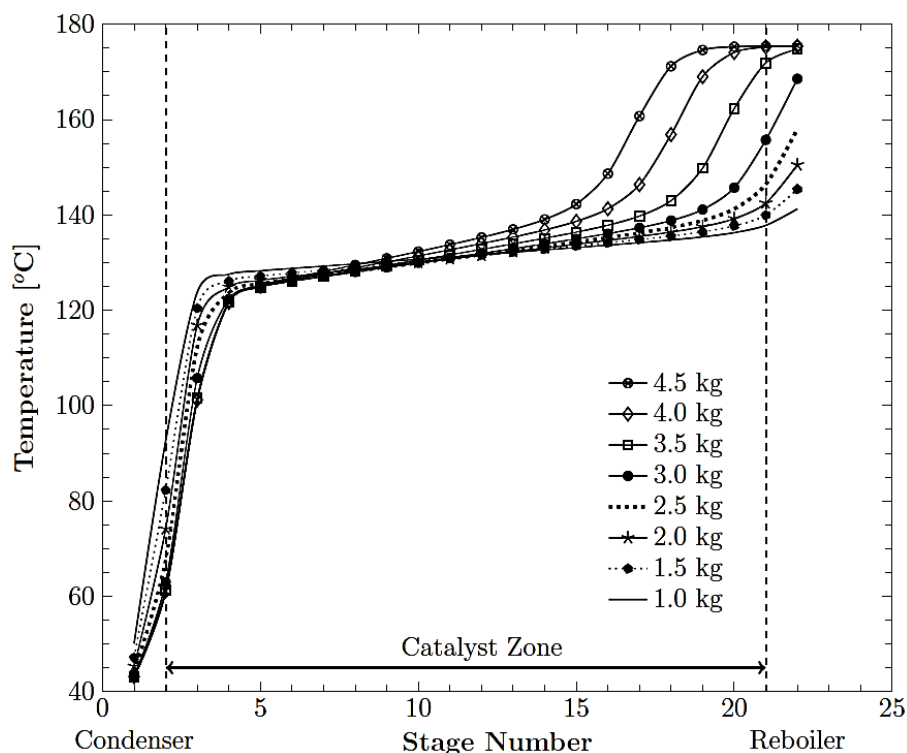
Figure 3.3: Effect of total catalyst loading on temperature profiles for a reflux ratio of 4, reboiler duty of 1.5 kW, and feed rate of 100 mol/h at 900 kPa

Figure 3.4 shows the methanol concentration in the bottom product stream and the DME concentration in the overhead product stream as a function of number of stripping sections added to the column. The addition of eight equilibrium stages (non-catalyst) to the stripping section reduces the bottom methanol concentration to less than 0.01 mol % while increasing the DME

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purity to 92 mol %. However, there was no significant improvement in the methanol and DME concentrations over eight equilibrium stages.
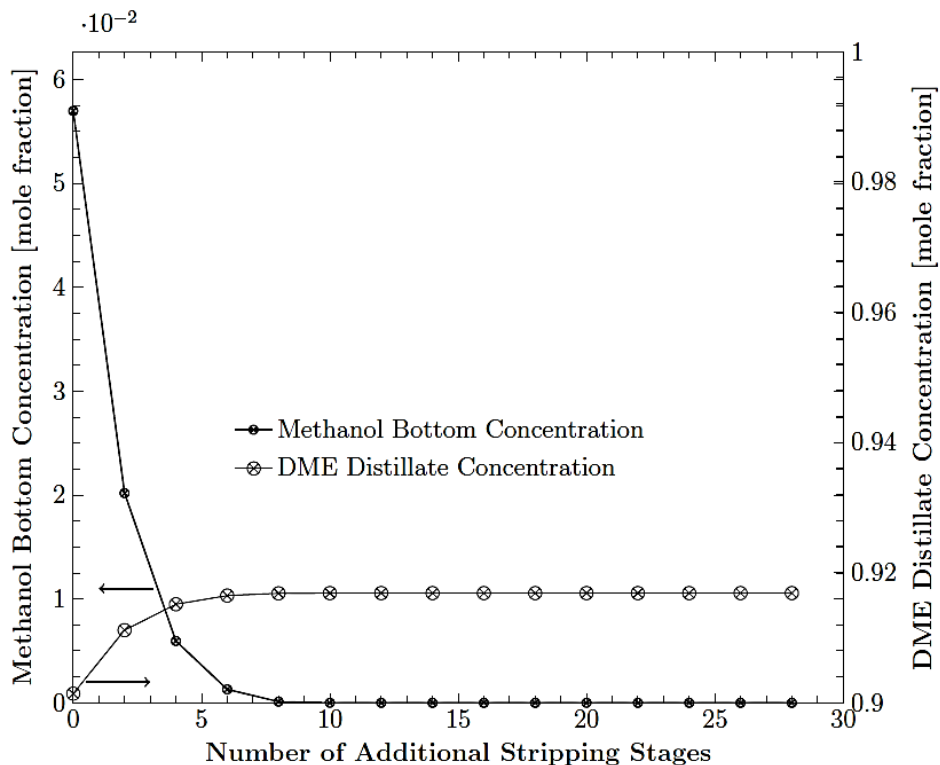
Figure 3.4: Effect of additional stripping stages on bottom methanol and distillate DME concentrations containing total of 2.8 kg of catalyst and reflux ratio of 4, reboiler duty of 1.5 kW, and feed rate of 100 mol/h at 900 kPa

From these preliminary simulations it was determined that a column with a total catalyst loading of 2.8 kg distributed across 20 stages and with eight stripping stages meets the target performance. As shown in Figure 3.5, the concentration of methanol in the reboiler is insignificant and the highest concentration of DME in the condenser was obtained without exceeding the temperature within the catalyst zone above 150 °C. With these starting specifications at a reflux ratio of 4, a reboiler duty of 1.5 kW, a column pressure of 900 kPa and a 100 mol/h feed rate a base case was formed. Using the values summarized in Table 3.2, the

following parameters were investigated: the reaction zone, reflux ratio, reboiler duty, feed stage location, column pressure, methanol concentration in the feed flow, feed stream temperature and feed flow rate. These parameters were varied independently.
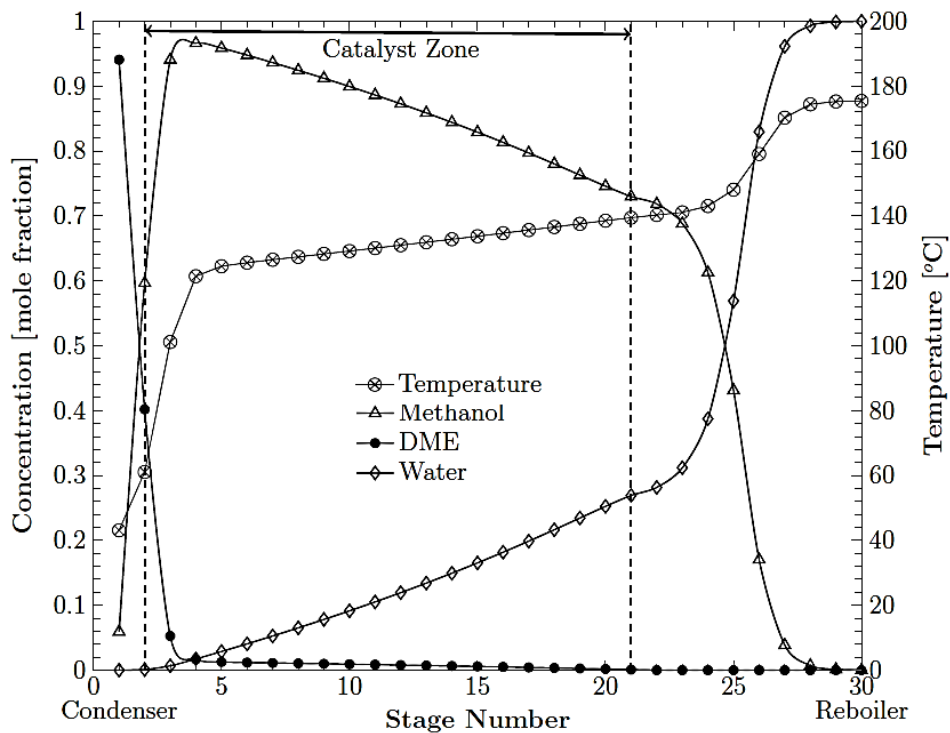
Figure 3.5: Concentration and temperature profiles for catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW, and feed rate of 100 mol/h at 900 kPa

Table 3-2: Summary of base case operating parameters

Feed Stream		CD Column	
Temperature:	298 K	Total Stages:	30
Pressure:	900 kPa	Rectification Stages:	None
Flow Rate:	100 mol/h	Reaction Stages:	2-21
Feed Composition:	Pure MeOH	Stripping Stages:	22-29
		Feed Stage:	2
		Total Catalyst Loading:	2.80 kg
		Catalyst Loading:	140 g/stage
		Column Pressure:	900 kPa
		Reflux Ratio:	4
		Reboiler:	1.5 kW

3.3 Reaction Zone

The catalyst bed on each stage in the reaction zone acts as a small liquid-phase reactor. By moving the reaction zone from the top of the column to the bottom stage by stage, we can determine the ideal place for the reaction zone to obtain the highest conversion and concentration of DME. Figure 3.6 shows the effect of varying the reaction zone location on the methanol and DME concentrations, as well as on the liquid-phase temperature profile. In these simulations, the size of the reaction zone and the total catalyst amount of 2.8 kg. Furthermore, the methanol feeding stage were kept constant at stage 2. The best place to put the reaction zone is between
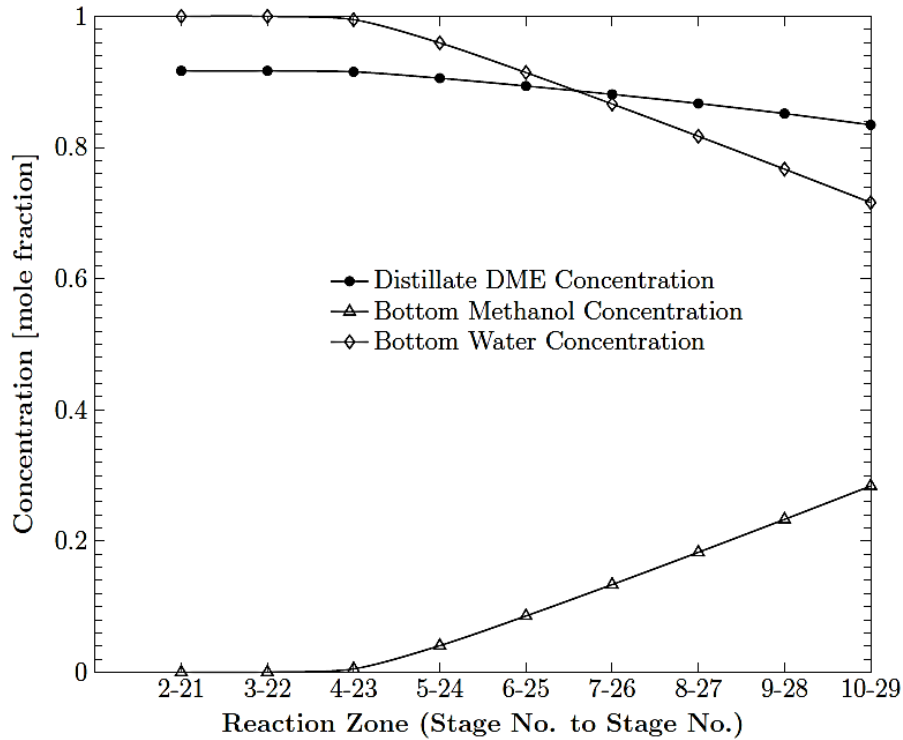
Figure 3.6: Effect of reaction zone location on distillate DME and bottom methanol concentrations for reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h and column pressure at 900 kPa

stages 2 and 21, where the DME concentration is the highest, while unreacted methanol in the bottoms is the lowest. The simulation results show that moving the reaction zone to the bottom of the column lowers the conversion of the methanol to the DME and increases the reaction zone temperature because of insufficient striping stages for the separation. The increase in the temperature is probably because the concentration of water increases as you approach the bottom of the column, which gives the mixture a higher boiling point.

The reaction zone is usually placed near the middle of the column to ensure sufficient stripping and rectifying zones. More rectifying stages give more separation of the light key component (DME) in the distillate and more stripping stages give a higher purity of the heavy key component (water) in the bottom stream. However, because water inhibits the reaction and gives

an increase in temperature, it is better to keep the reaction zone where the concentration of water is the lowest. Figure 3.5 shows that the water concentration begins to increase rapidly after stage 23, and to avoid high water concentration, the reaction zone was placed near the top, away from the large increase in water concentration. Column temperatures are the highest near the reboiler, therefore reaction zones are more prone to deactivation by exceeding catalyst operating temperatures if placed closer to the reboiler.

3.4 Reflux Ratio

Subawalla and Fair, (1999) indicated that reflux ratio affects both reaction rate and separation performance in a catalytic distillation column. Figure 3.7 shows the reflux ratio effect on the distillate DME concentration and the methanol concentration in the bottom product stream for a catalyst loading of 2.8 kg, reboiler duty of 1.5 kW, feed rate of 100 mol/h and a pressure of 900 kPa. At higher reflux ratios, methanol recycle increases inside the reaction zone, leading to an increase in local methanol concentration, which further drives the reaction forward. Furthermore, increasing the reflux increases the separation efficiency and consequently the purity of the DME concentration distillate stream. It can be seen in Figure 3.7 that increasing the reflux improves conversion and DME purity in the distillate. However, Figure 3.7 also shows that increasing reflux ratio increases the methanol concentration in the bottom product stream. This is because at the higher reflux ratio the local methanol concentration in each reaction zone increases, which lowers the liquid phase temperature and consequently reduces the conversion of DME. Figure 3.8 shows that as the reflux ratio increases the temperature each reaction zone decreases. Increasing the reflux ratio also results in higher operation costs for both condenser and reboiler while the column diameter will need to be increased to accommodate higher flow traffic inside

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the column. Therefore, the optimum operating reflux ratio was determined to be 4 due to flooding for catalyst loading of 2.8 kg, reboiler duty of 1.5 kW and feed rate of 100 mol/h and the tower pressure at 900 kPa.
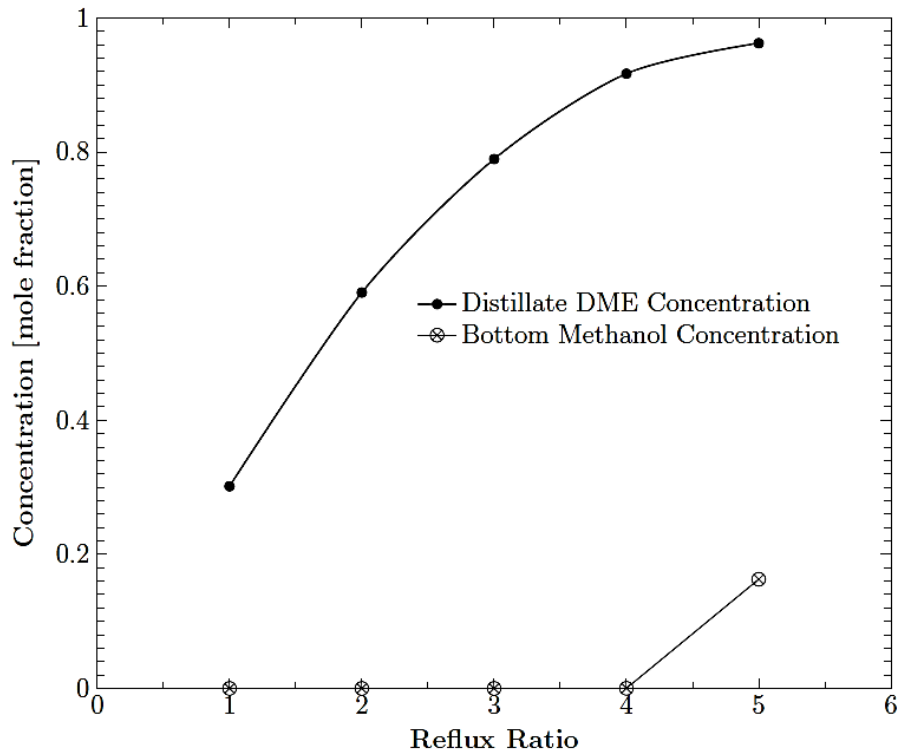
Figure 3.7: Distillate DME and bottom methanol concentrations at varying reflux ratios. Catalyst loading of 2.8 kg, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa.
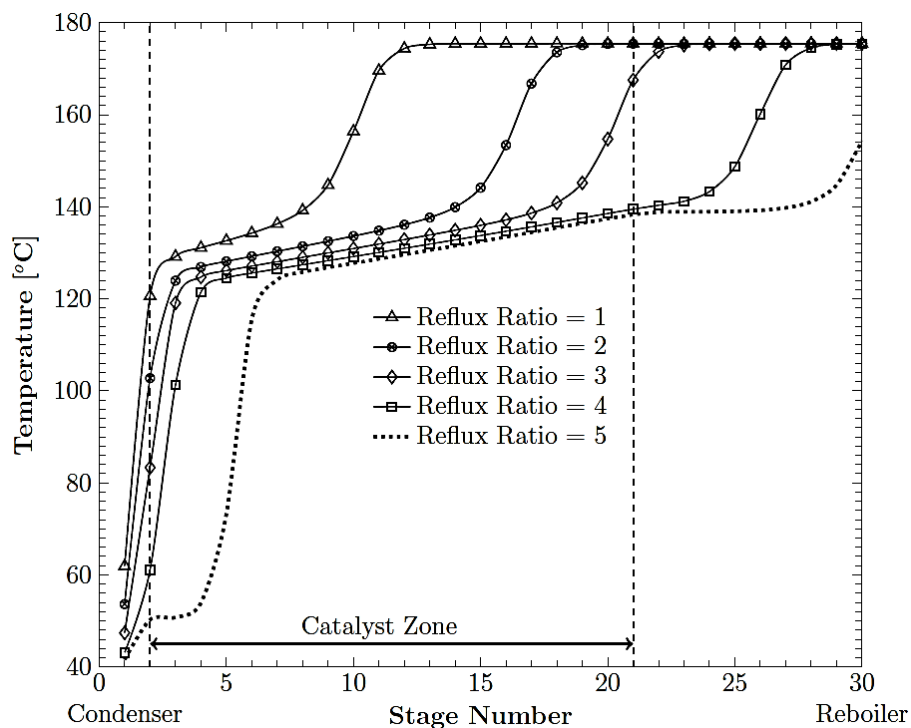
Figure 3.8: Column temperature profiles at varying reflux ratios. Catalyst loading of 2.8 kg, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa.

3.5 Reboiler Duty

Increasing the reboiler duty or boil-up rate increases fluid traffic inside the column due to the increased vapour flow. A series of simulations was performed, with a total catalyst loading of 2.8 kg, reflux ratio of 4, pure methanol feed rate of 100 mol/h and column pressure of 900 kPa. The reboiler duty (boil up rate) was varied between 1.5 and 4.0 kW. Figure 3.9 shows the effect of the reboiler duty on the DME and methanol concentrations in the distillate and bottom product streams. Increasing the reboiler duty lowers the concentration of DME in the distillate. The decrease in the DME concentration might be caused by the reaction rate and the separation efficiency. At higher reboiler duties, the water concentration in the liquid-phase in the reactive zones of the column increases. As Hosseininejad et al., (2012) stated, higher water concentrations inhibit catalytic methanol dehydration to DME over ion exchange catalyst resin.

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Water and methanol molecules compete for adsorption at catalytic active sites on the surface of acid catalyst. Therefore, the concentration of DME concentration decreases in the distillate stream as the reboiler duty increases. Furthermore, Figure 3.10 shows that increasing the reboiler duty increases the liquid-phase temperature profile across the column, which can cause the catalyst to deactivate at temperatures greater than 150 °C. Therefore, it is concluded that for the total catalyst loading of 2.8 kg, reflux ratio of 4, pure methanol feed rate of 100 mol/h and the column pressure at 900 kPa the reboiler duty (boil up rate) should be kept at 1.5 kW to ensure the highest possible the DME concentration in the distillate stream and the lowest methanol concentration in the bottom product stream.
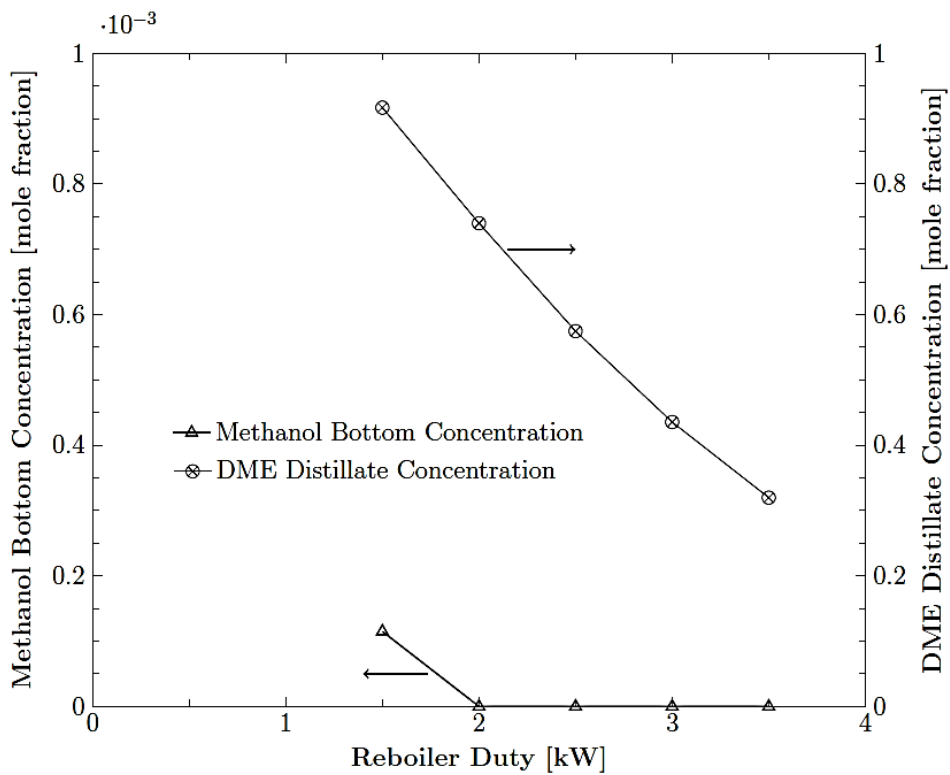
Figure 3.9: Effect of reboiler duty on the DME and methanol concentrations in the distillate and bottoms product streams for total catalyst loading of 2.8 kg, reflux ratio of 4 and feed rate of 100 mol/h at 900 kPa

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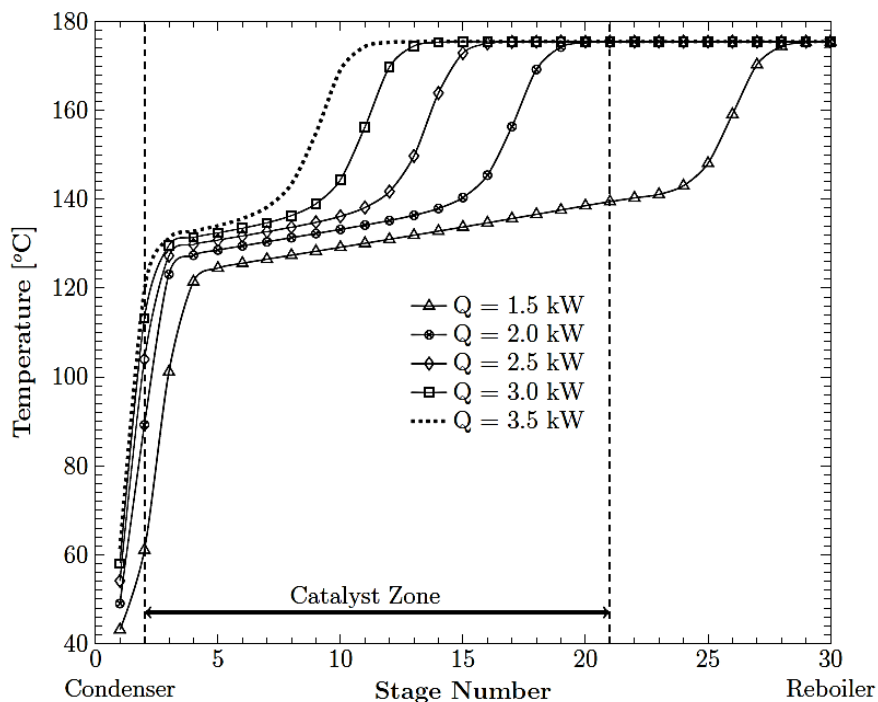
Figure 3.10: Effect of reboiler duty on column temperatures. Catalyst loading of 2.8 kg, reflux ratio of 4 and feed rate of 100 mol/h at 900 kPa

3.6 Feed Stage Location

As with conventional distillation columns, the feed stage location affects the performance of the catalytic distillation column. The optimum feed location depends on product specification, volatility of components and vapour-liquid equilibrium behaviour. For this reaction, the water product has a higher boiling point than methanol. Furthermore, if a low methanol concentration is required in the bottom product, the feed location should be at the upper portion of the column to increase the stripping section. As discussed in Section 3.3, the best place to put the reaction zone is between stages 2 and 21 where DME concentration is the highest, while methanol in the bottoms is the lowest. Figure 3.11 shows the effect of feed stage location on purity of DME in the distillate stream and the methanol concentration in the bottoms product stream for the total catalyst loading of 2.8 kg, reflux ratio of 4, pure methanol feed rate of 100 mol/h, column

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pressure of 900 kPa and the reboiler duty (boil up rate) at 1.5 kW. The optimum feed stage location was determined by varying that location between stages 2 to 29 while keeping the reaction zone constant between stages 2 and 21. The DME concentration in the distillate stream was maximized and the methanol concentration was minimized by feeding the pure methanol just above the reaction zone, between stages 2 and 6. The reaction rate is the highest because the reaction product of water and DME are removed from the reaction right away, which maximized catalytic methanol dehydration to DME. Figure 3.11 also shows that when pure methanol feed is at the bottom of the reaction zone or even lower than the reaction zone the conversion of methanol is reduced and leads to lower purity of the DME in the distillate stream. Therefore, the optimum location for pure methanol feed should be just above of the reaction zone, on stage 2.

Figure 3.11: Effect of feed stage placement on distillate DME and bottom methanol concentrations for total catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa

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3.7 Column Pressure

Hosseininejad et al. (2012) showed that Amberlyst 35 ion exchange catalyst had significant activity and selectivity in the temperature range of 110 – 135 °C, which is favourable for DME and methanol-water separation. Furthermore, the manufacture specification sheet indicates that the maximum allowable temperature is 150 °C, above which temperature the catalyst will rapidly lose activity and selectivity. Therefore, the temperature throughout the column is critical with the use of ion exchange catalyst such as Amberlyst 35. Higher temperatures increase the rate of reaction and in turn increase conversion in catalytic distillation but too high temperatures deactivate the catalyst. The low temperature dehydration of methanol to DME is preferred to ensure that the catalyst (Amberlyst 35) does not lose its activity and selectivity and to reduce capital and operating costs of reactive distillation column. The temperature profile across such columns can be reduced by lowering column operating pressure. The effect of column pressure on the DME concentration in the distillate stream and the methanol concentration in the bottom product stream, and temperature profile are shown in Figures 3.12 and 3.13, respectively. These simulations were conducted while the total catalyst loading of 2.8 kg, reflux ratio of 4, pure methanol feed rate of 100 mol/h, reboiler duty of 1.5 kW and the column pressure at 900 kPa were kept constant. Lowering the column pressure from 900 kPa to 700 kPa, lowers the temperature profile throughout the column. However, Figure 3.12 shows that decreasing the pressure lowered the conversion and purity of DME in the distillate product along with substantial increased concentrations of unreacted methanol in the top and bottom product streams. Therefore, it was concluded that the column pressure should not be lower than 800 kPa

to ensure reasonably high purity of DME and as low as possible methanol concentration in the

bottom product stream.
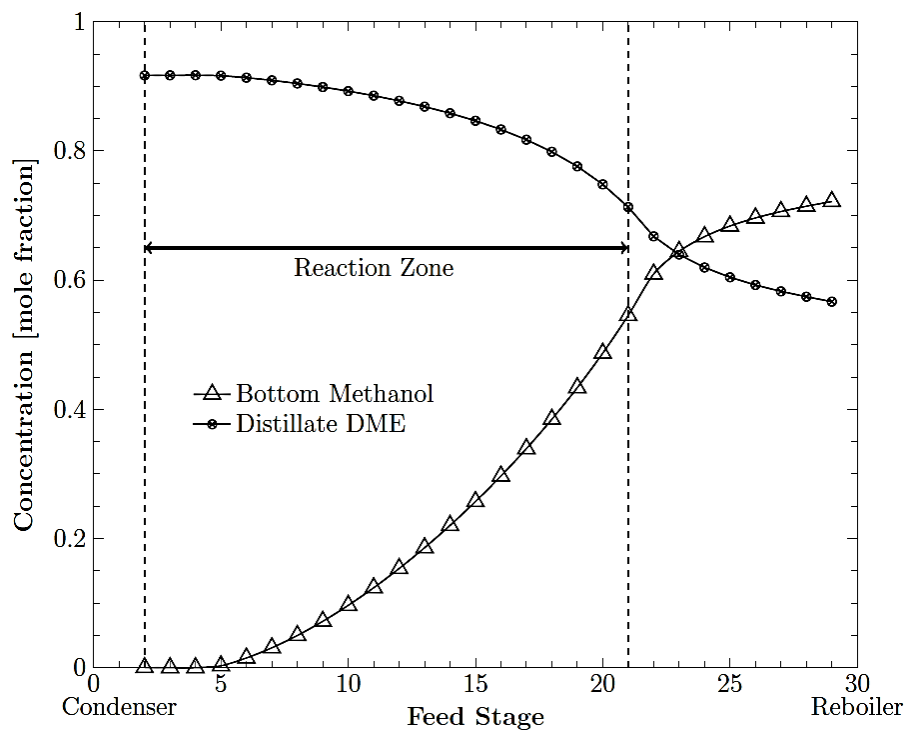

Figure 3.12: Effect of column pressure on distillate DME and bottom methanol concentrations. Catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h

Figure 3.13: Effect of varying column pressure on temperature profiles. Catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h

3.8 Methanol Concentration in Feed Stream

DME can be produced from methanol via synthesis gas, which in turn can be produced from a variety of sources such as biomass, residual oil, crude oil, coal, natural gas, forest products, agricultural by-products, fuel crops and municipal waste (Fang et al, 2011). However, a source that can produce synthesis gas that is further converted to methanol might contain impurities such as water. Weizhu et al., (2004) and Hosseininejad et al., (2012) studies confirmed that the presence of water inhibits catalytic methanol dehydration to DME over acidic ion exchange resin catalysts. Therefore, a series of simulations were conducted to study the effect of presence of water content in the feed on the DME concentration in distillate stream and temperature profile in the reaction zone. These simulations were conducted while the total catalyst loading of 2.8 kg, reflux ratio of 4, pure methanol feed rate of 100 mol/h, reboiler duty of 1.5 kW and the column

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pressure at 900 kPa were kept constant. Figure 3.14 shows the effect of methanol concentration in feed on DME and temperature in the reaction zone. As methanol concentration in the feed stream decreases the DME purity in the distillate stream decreased as expected. Water and methanol compete for adsorption at catalytic active sites on the surface of acid catalyst, which leads to higher temperatures reaction zone, which leads to deactivation of the catalyst. Lower methanol concentrations in the feed stream do not have any effect on the methanol concentration in the bottom product stream.
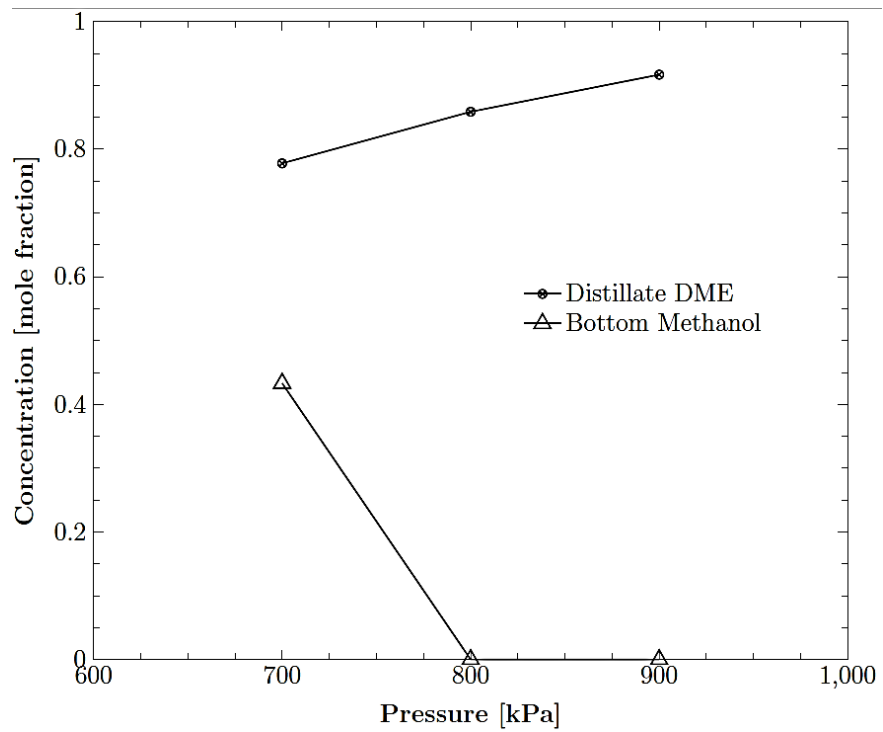

Figure 3.14: Effect of feed concentration on distillate DME and bottom methanol concentrations. Catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa

3.9 Feed Temperature

The effect of feed temperature on the DME concentration in the distillate stream and methanol concentrations in bottom product stream as well as temperature profile across the column were also examined by varying pure methanol feed stream temperature between 15 - 55 °C. These simulations were conducted while the total catalyst loading of 2.8 kg, reflux ratio of 4, pure methanol feed rate of 100 mol/h, reboiler duty of 1.5 kW, the column pressure at 900 kPa and the feed location at stage 2 were kept constant. Figures 3.15 shows that as feed stream temperature increases the purity of the DME decreases, but does not have significant effect on the methanol concentrations. The feed stage is above the reaction zone, at stage 2. As the feed stream temperature approaches to the dew-point of pure methanol, some of the methanol partially vaporized and increases vapour rate, which decreases the purity of the DME in the distillate stream. As expected, Figure 3.15 also shows that an increase in the feed stream temperature has insignificant effect on the methanol concentration in the bottom product stream. Figure 3.16 shows the effect of the feed stream temperature on the temperature profile across the column. Increasing the feed stream temperature had no significant effect on the temperature profile remains constant before and within the reaction zone. As expected, after the reaction zone the temperature profile increases with higher temperature feeds.
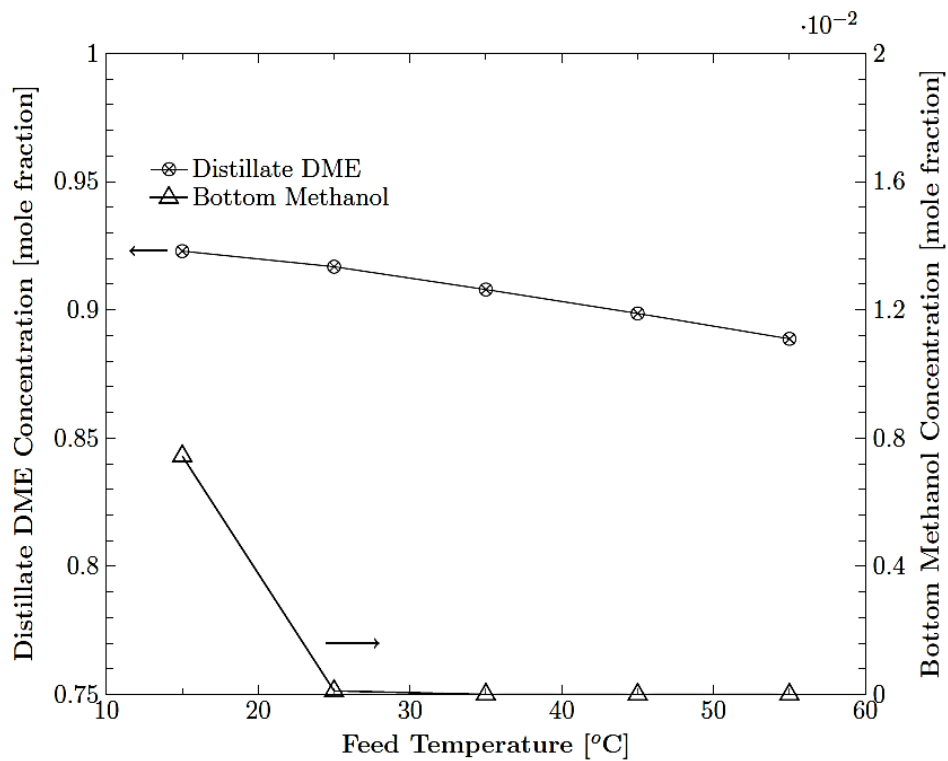
Figure 3.15: Effect feed stream temperatures on distillate DME and bottom methanol concentrations for catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa
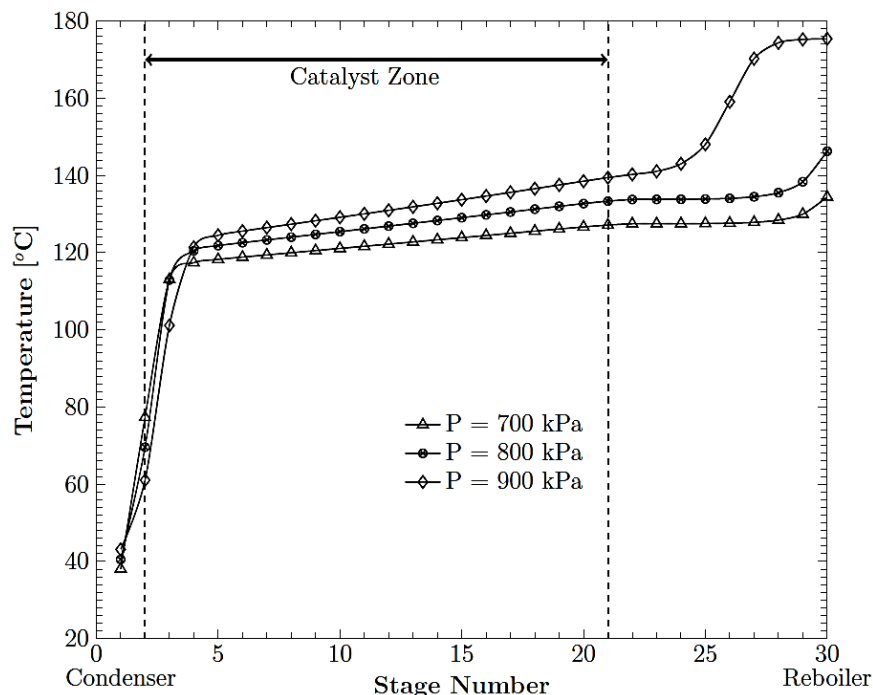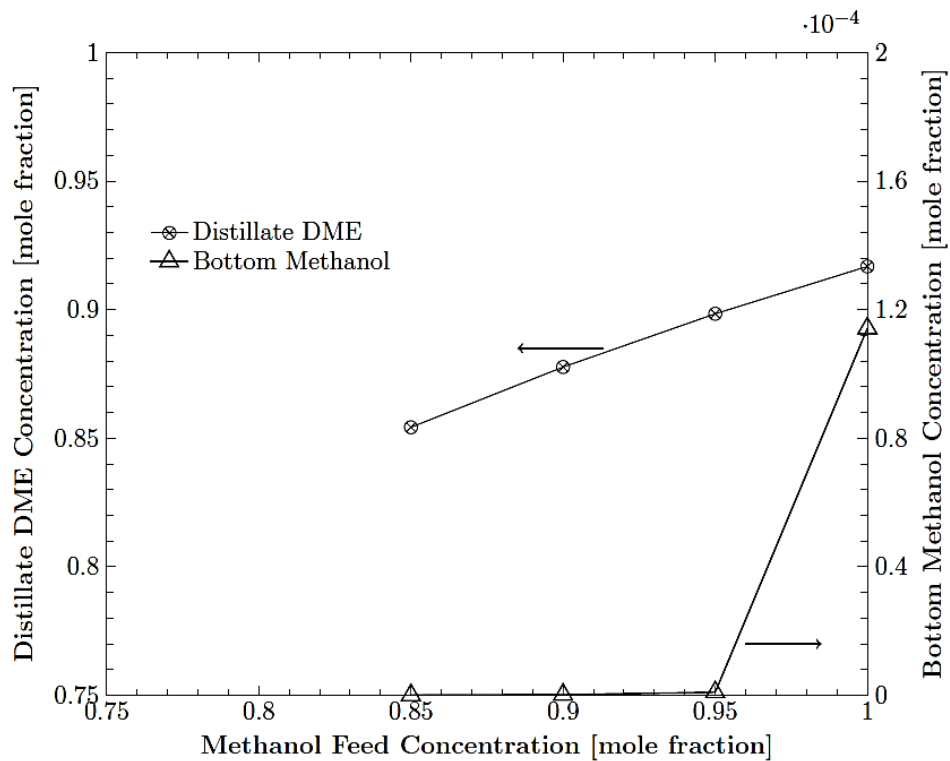
Figure 3.16: Effect of feed temperature on column temperature profiles for catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and feed rate of 100 mol/h at 900 kPa

3.10 Feed Rate

In a catalytic distillation column with a fixed number of stages, reflux ratio, catalyst loading per stage, size and the location of the reaction zone, reboiler duty and tower pressure, the methanol feed flow rate can only vary by a limited amount, due the capacity of the liquid/vapour traffic inside the column. Figures 3.17 and 3.18 show the effect of increasing pure methanol feed rate on the DME and methanol concentrations in the distillate and bottom product streams and temperature profile across the column, respectively. For these simulations, the pure methanol feed flow rate was varied from 40 mol/h to 180 mol/h while total catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and the column pressure of 900 kPa were kept constant. For pure methanol feed rates of 40 mol/h and 80 mol/h, the purity of DME is lower. This is due

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to the higher temperature in the reaction zone. Figure 3.18 shows that for feed rates 40 and 80 mol/h, the temperatures in the reaction zone are above than the maximum allowable temperature is 150 °C, which the catalyst will rapidly lose activity and selectivity. For pure methanol feed rates above 100 mol/h, the concentration of DME in the distillate stream remains constant at 0.95 mole fraction but the methanol concentration increases drastically in the bottom product stream. Increasing the feed rate, not only increases the vapour/liquid traffic inside the column but also shortens residence time for methanol dehydration to DME. From these simulations It is evident that the reactive distillation column with fixed of number of stages, reflux ratio, total catalyst amount, size of the reaction zone, reboiler duty, reflux ratio and column pressure is design to operate at a limitation with methanol feed rate of 100 mol/h.
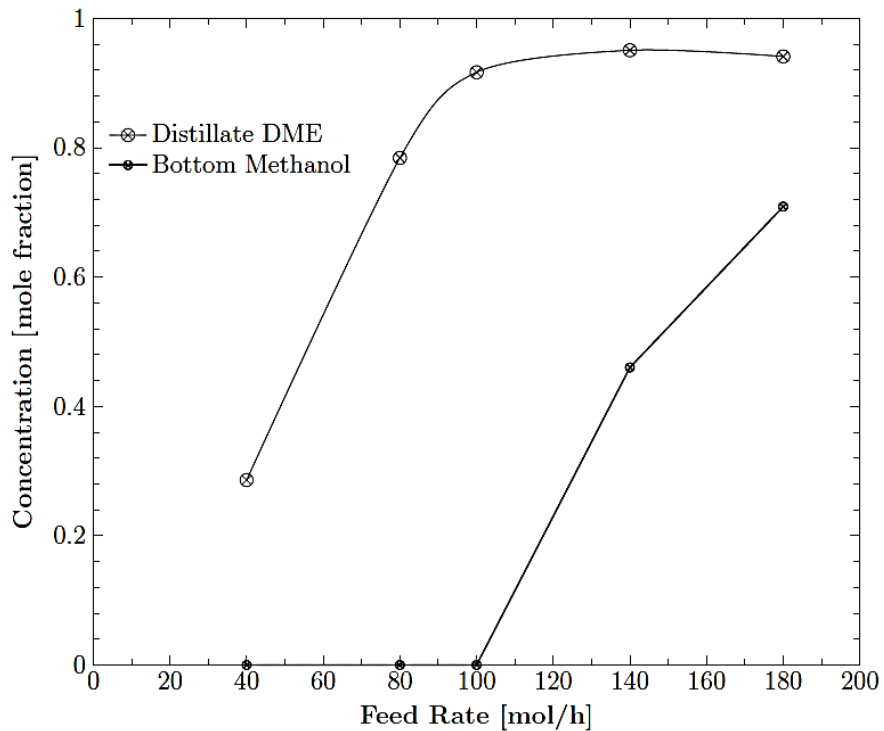
Figure 3.17: Effect of feed rate on product concentrations for total catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and column pressure of 900 kPa
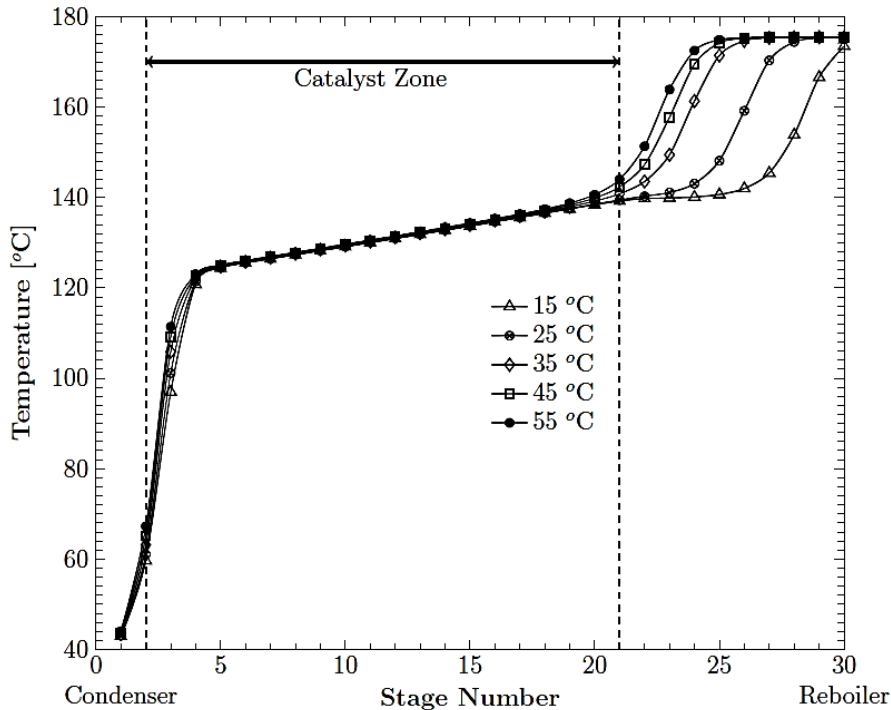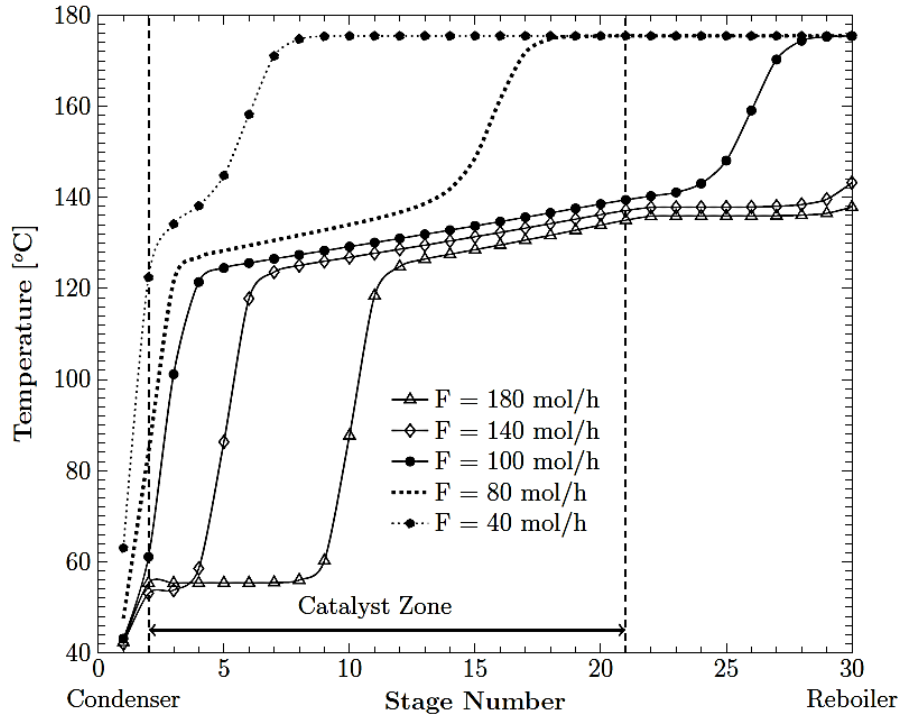
Figure 3.18: Effect of feed rate on column temperature profile. Catalyst loading of 2.8 kg, reflux ratio of 4, reboiler duty of 1.5 kW and column pressure of 900 kPa

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Chapter 4

Conclusions and Recommendations

The objective of this study was to conduct a parametric study by incorporating a previously published kinetic model into the commercial simulation program Aspen Plus to determine operating strategies for the dehydration of methanol to dimethyl ether using catalytic distillation. In the study, parameters such as number of equilibrium stages, total catalyst loading, catalyst location, reflux ratio, reboiler duty, feed rate, feed location, feed concentration, feed temperature and column pressure were examined. The parametric studies and operating strategies were conducted for 2 inches (5.08 cm) diameter column. The following conclusions were obtained:

- Parametric studies showed that the optimum total catalyst loading was 2.8 kg, the column should have a total of 30 theoretical equilibrium stages with eight stripping stages, the reaction zone should be placed at the top of the column between stages 2-21, the column should be operated between 800 and 900 kPa with reflux ratio of 4 for 100 mol/h pure methanol feed rate entering the column just above the reaction zone and reboiler duty of 1.5 kW to achieve the highest DME purity in the distillate stream and the lowest methanol concentration in the bottom product stream.

The simulation results from Aspen Plus provided a strong insight on the operations of a catalytic distillation column to produce dimethyl ether from methanol. However, the successful designing and optimizing of a catalytic distillation process poses several challenges, which include the determination of appropriate reaction kinetics, all the aspects of column selection, including column internals design with optimum combination as well as hydraulic and mass transfer characteristics and operating limitations. In the open literature, there are no published

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experimental data for DME production using catalytic distillation process. To verify simulation results, it is recommended a pilot plant scale reactive distillation column should be built to obtain mass transfer (i.e. component tray efficiency) and hydraulic characteristics of the catalytic distillation column. The experimental data then can be used to validate simulation results and allows us to design catalytic distillation columns to produce DME from methanol with confidence.

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APPENDIX

Appendix A: Aspen Plus Catalytic Distillation for DME Production Tutorial

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By: Danish Dar

- Determining distillate and bottom product flows and compositions in a catalytic distillation unit for the production of dimethyl ether using methanol dehydration

<u>Setting up the Model</u>

1. In the FILE toolbar, click NEW

2. Under BLANK AND RECENT, select BLANK SIMULATION and click CREATE
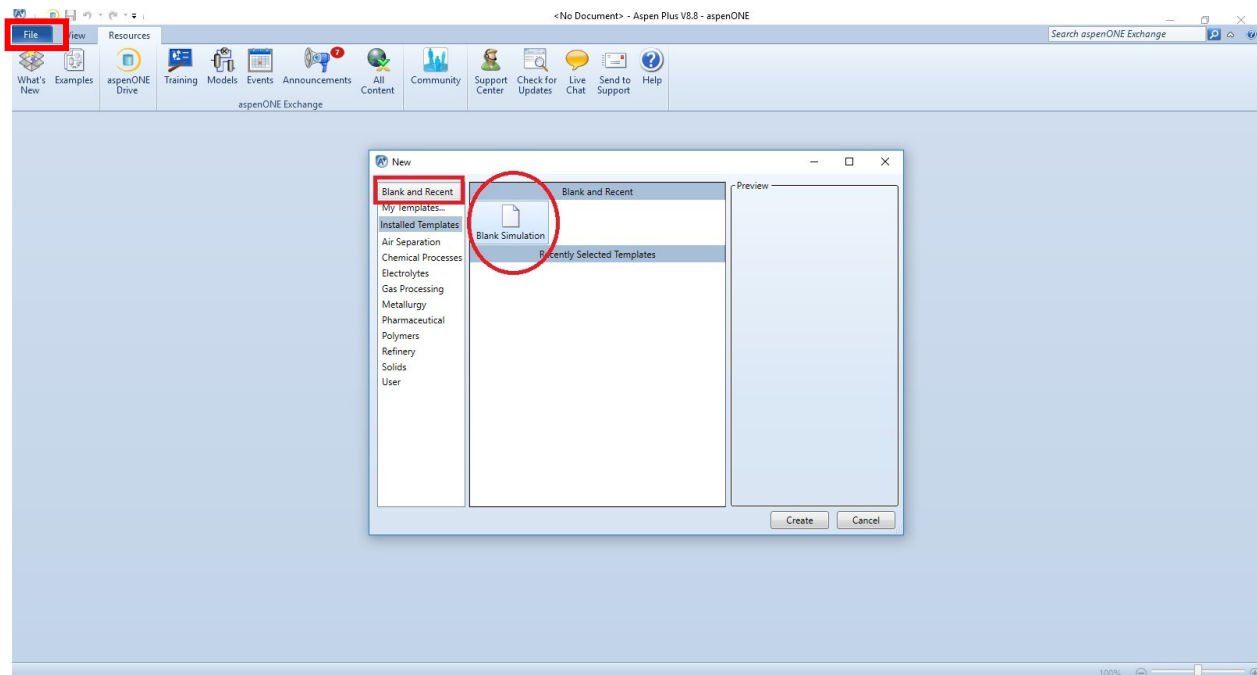
3. Once a new template is opened, the first window should be the COMPONENTS window. If not, in the window pane on the bottom left hand side select PROPERTIES then expand the COMPONENTS folder on the left PROPERTIES pane and select SPECIFICATIONS

4. In this section, we need to input all the chemical compounds that will be present in the simulation, in this example methanol will dehydrate to form water and dimethyl ether so we have three components to enter

Reaction is: $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
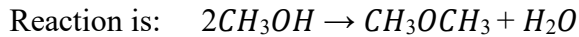
5. Click FIND and search the components required in the simulation, you can either search using the standard name or by its chemical structure (e.g CH4O for Methanol)

6. Once all components required for the simulation have been entered you can either click NEXT on HOME toolbar which takes you to the next required input to complete the simulation. The next required input should be the selection of a thermodynamics package in METHODS. To get there manually expand the METHODS folder on the left PROPERTIES panel and select

SPECIFICATIONS

7. This is a very important step as the wrong thermodynamics package can lead to incorrect results in your simulation and should be determined before beginning your simulation. You can click on the METHODS ASSISTANT button which will ask you a series of questions on the properties of the components you have chosen in step 4 and help you determine the property package best suited for your components. Under BASE METHOD select the appropriate thermodynamic package from the dropdown menu. In this example NRTL method is chosen as the best thermodynamic package for this simulation.
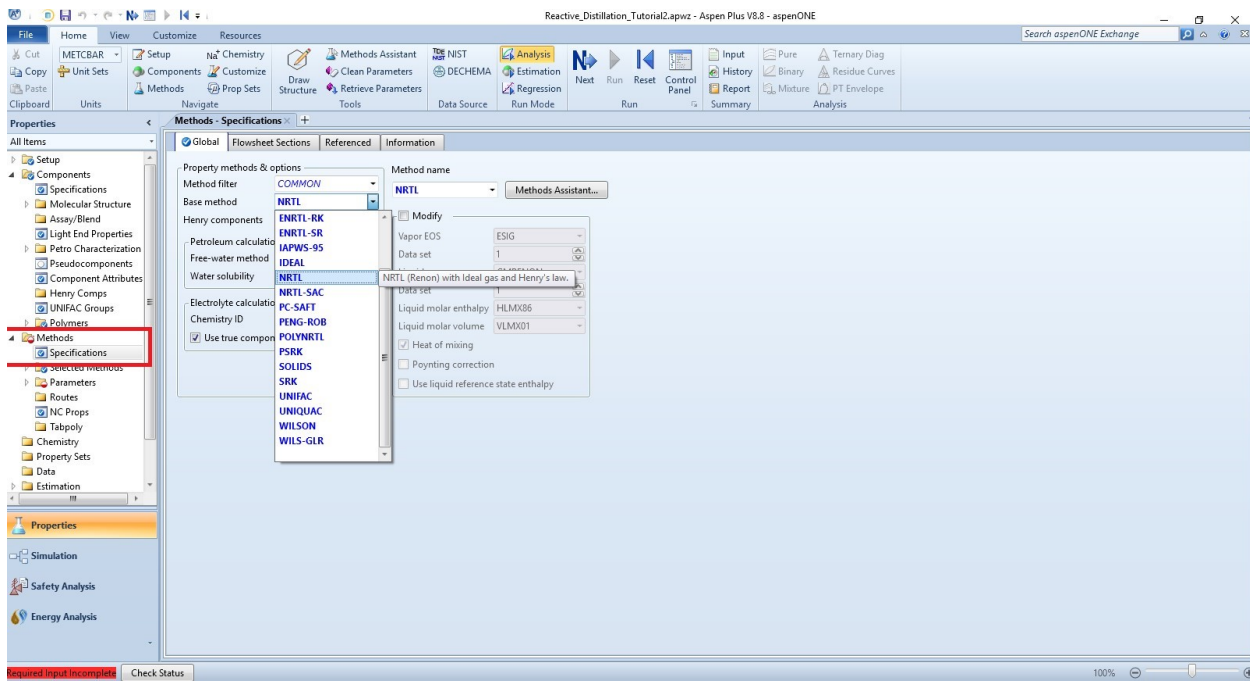
8. By clicking NEXT Aspen Plus will take you to the BINARY INTERACTION PAGE to review the parameters Aspen Plus has set or to manually change property parameters. In this case, no changes were made
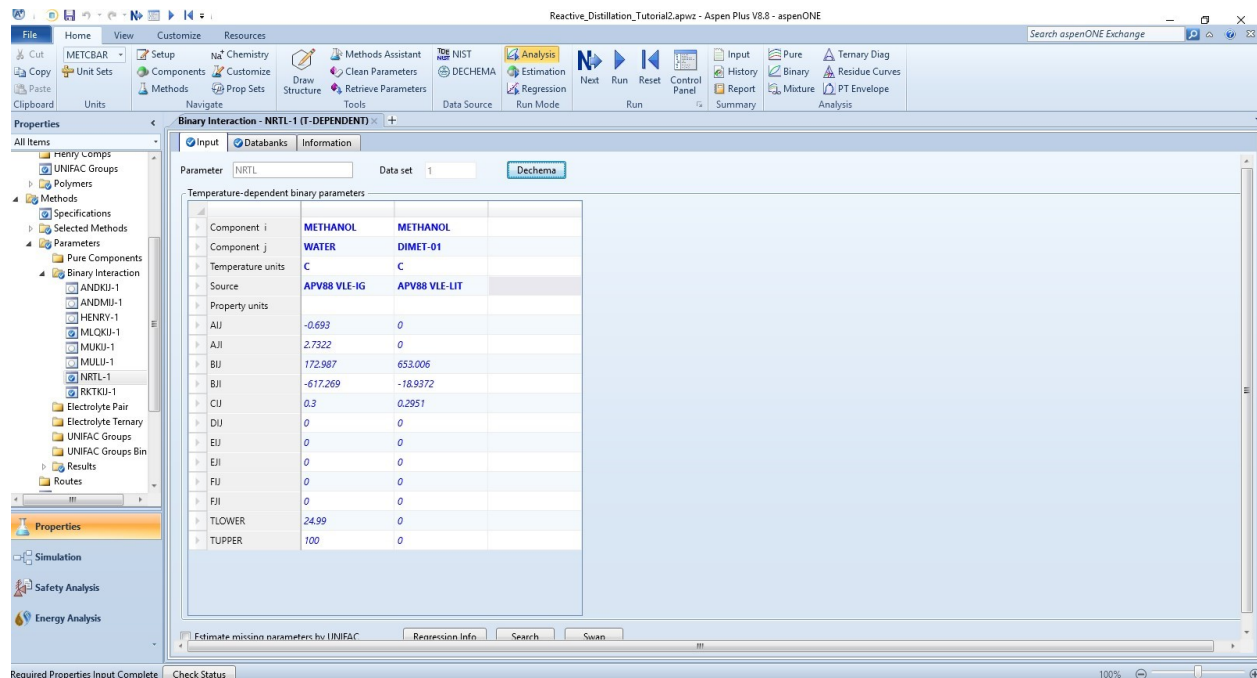
9. By clicking NEXT a pop-up window will appear asking for your next step, select RUN
   PROPERTY ANAYLSIS. Once that is complete you should get a message saying "Table
   generation complete." Now enter the simulation environment by clicking SIMULATION in
   the bottom left
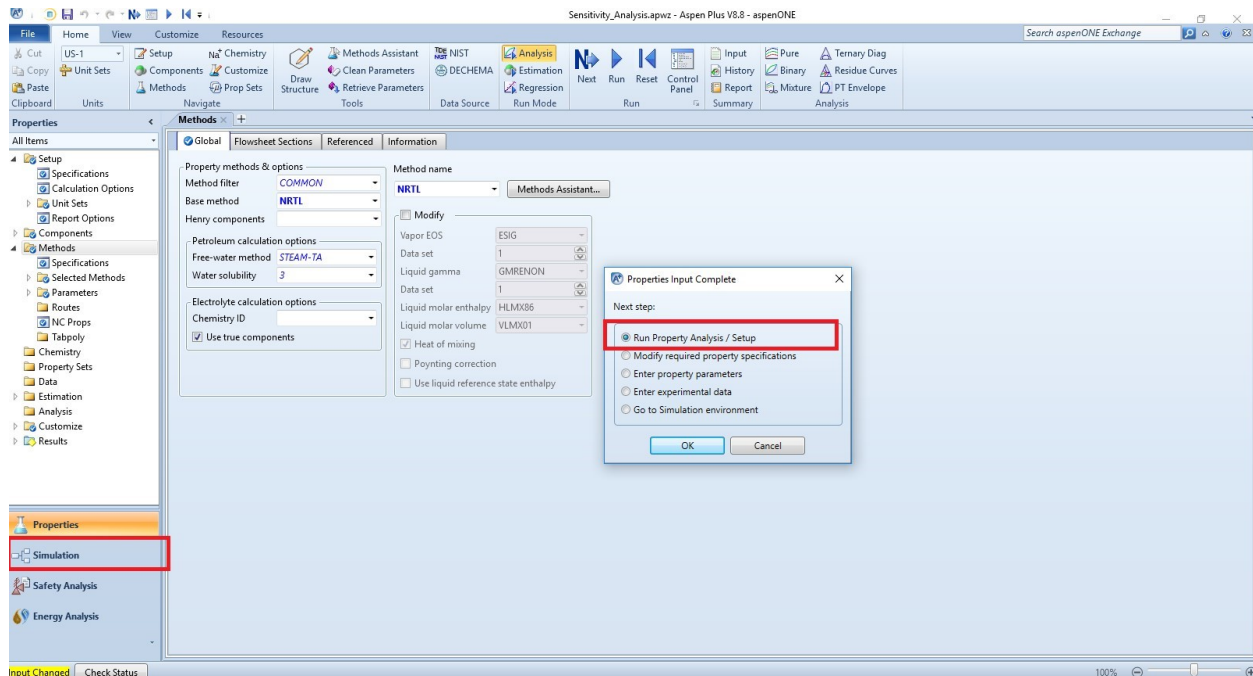
10. Once you enter the simulation page, you should see a blank canvas with a MODEL PALETTE at the bottom with different process units to choose from. If you do not see the MODEL PALETTE you can display the palette by going to the VIEW toolbar and selecting MODEL PALETTE in the SHOW section

11. In the MODEL PALETTE click on the columns section, select the RADFRAC box (distillation column). The dropdown menu beside the box shows different orientations of the distillation column available, for this example the FRACT1 orientation is appropriate. The mouse will change to a crosshair once RADFRAC is selected, now click anywhere on the blank canvas to place the distillation column

12. Once the unit has been placed, right click to get rid of the crosshair or click on the black mouse button at the top left of the MODEL PALETTE. Now material streams can be added by selecting the MATERIAL STREAMS box on the left, red and blue arrows will appear around the distillation column. RED arrows represent material streams that are mandatory for

the simulation and BLUE arrows represent material streams that are optional. Some arrows will turn BLUE when some conditions are met. For example, there are two RED arrows exiting the condenser but once you specify a vapor or liquid distillate the other arrow will turn BLUE. Click once on the RED arrows and drag the mouse away and click again to draw your materials streams, connecting them to the unit.

Make sure all required streams are connected to the process unit.
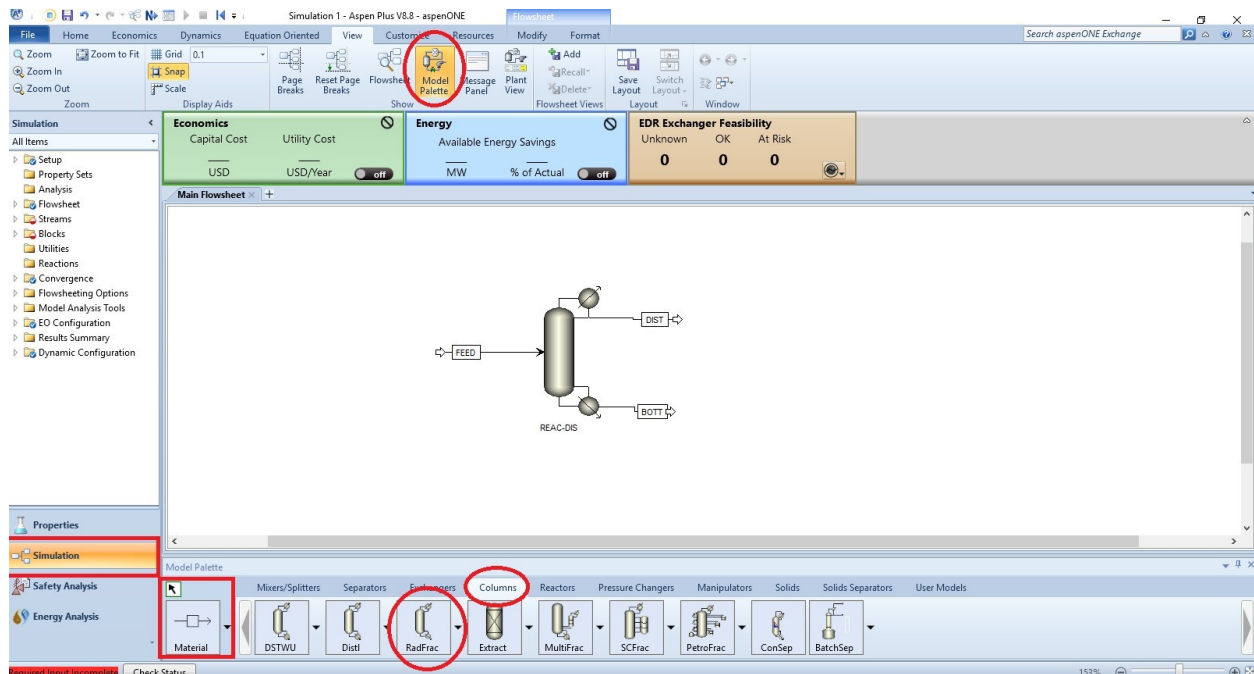
13. All unit blocks and streams can be renamed by double-clicking on the respective labels. All unit blocks and streams can be resized and moved by simply dragging the picture or corner points.

14. Once all the process units and streams are connected on the main flowsheet, click NEXT or go to STREAMS>FEED (depends on what you named your feed stream)>INPUT on the left SIMULATION PANEL. Here you must specify two of the following, either temperature,

pressure, or vapor fraction along with stream flowrates. In this example temperature and pressure is 300 K and 0.806 MPa, respectively. Use the dropdown menus to change the units of the input.

15. Next, we specify the total flow, which in this example is 50,000 kg/hr of pure methanol. Since we know it is pure methanol MASS-FRAC composition is selected from the COMPOSITION dropdown menu and a value of 1 is inputted for METHA-1 which signifies methanol
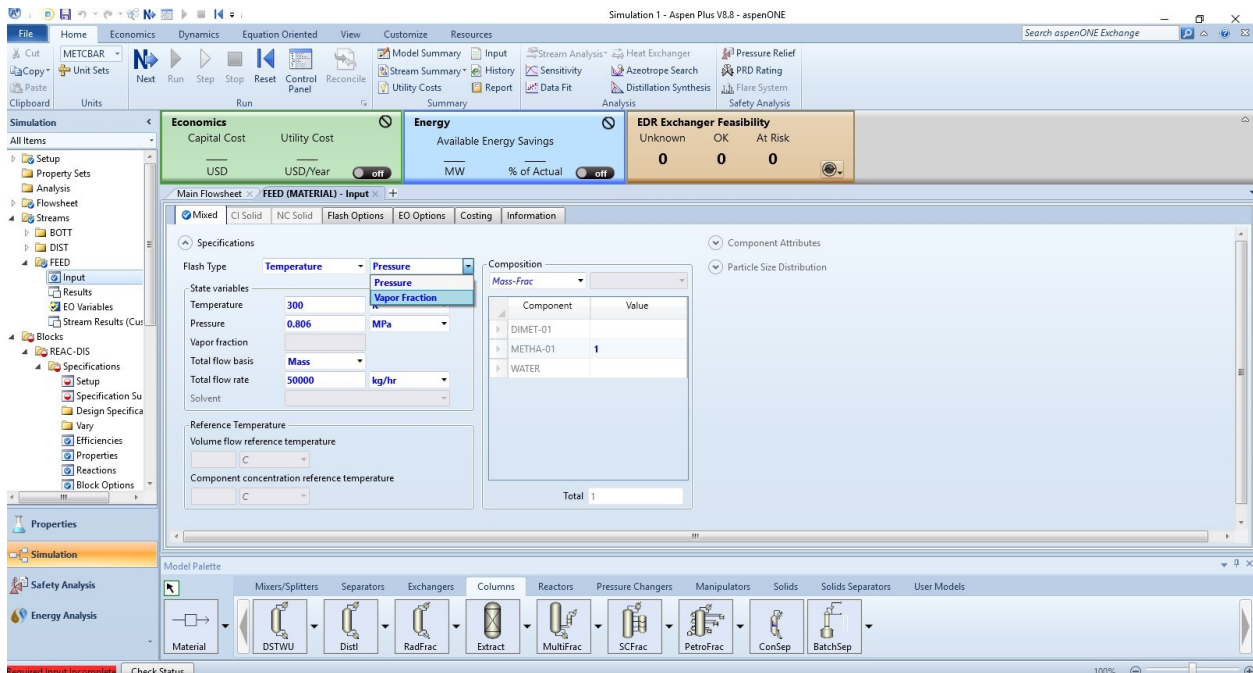
16. If you have multiple feed streams, steps 14 & 15 are repeated for each inlet stream
17. Click NEXT or on the left side SIMULATION panel and go to BLOCKS>REAC-DIS (Depends on what you named your process unit)>SPECIFICATIONS>SETUP. Here you will be required to enter if your distillation uses rate-based or equilibrium calculations, the number of stages, type of condenser, reboiler, component phases, type of convergence, and

two known degrees of freedom (e.g reflux ratio, distillate to feed ratio, distillate rate, etc…).

In this example we will use equilibrium, 50 stages, total condenser, kettle reboiler, vapor-liquid phase, standard convergence, reboiler duty of 42,017 kW, and a molar reflux ratio of 9.
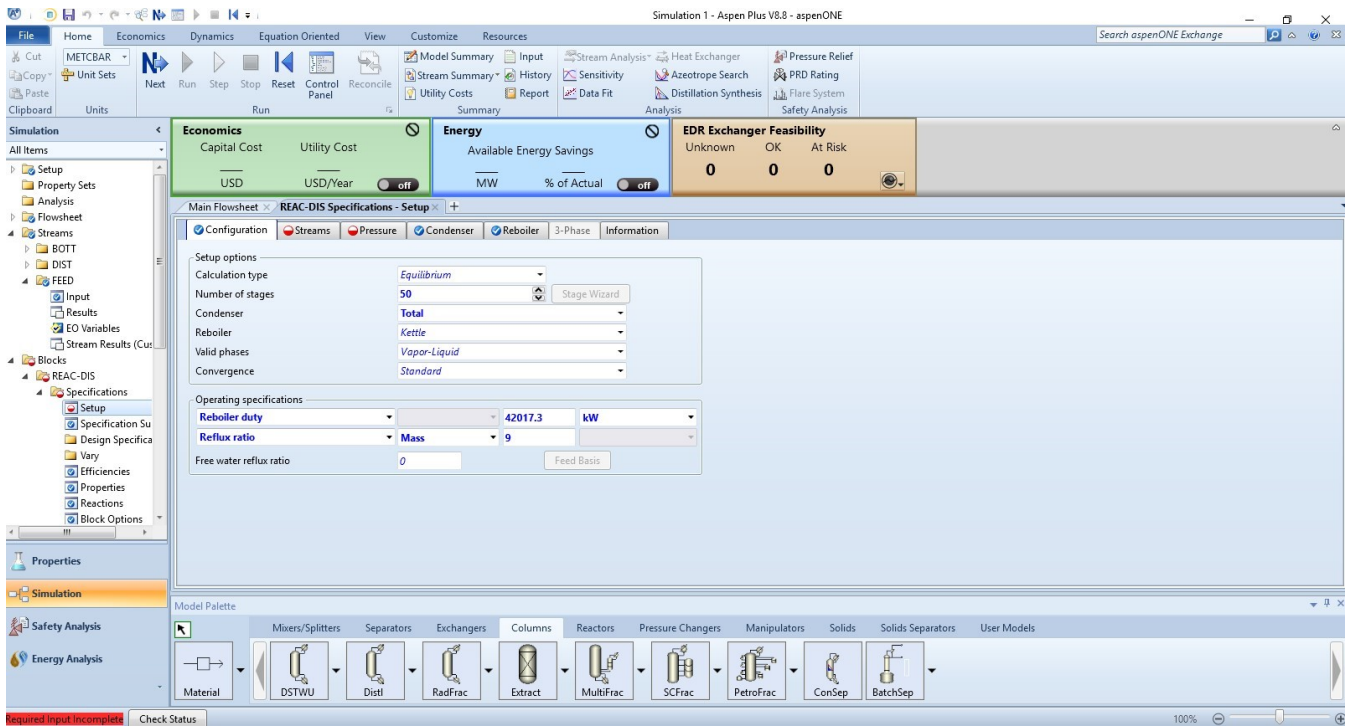
18. Click NEXT or click on the STREAMS tab, here we specify which stage the feed stream will enter, and which stages the products will exit. In this example, the methanol feed stream enters at stage 6 and products are withdrawn from the condenser (stage 1) and the reboiler (stage 50).
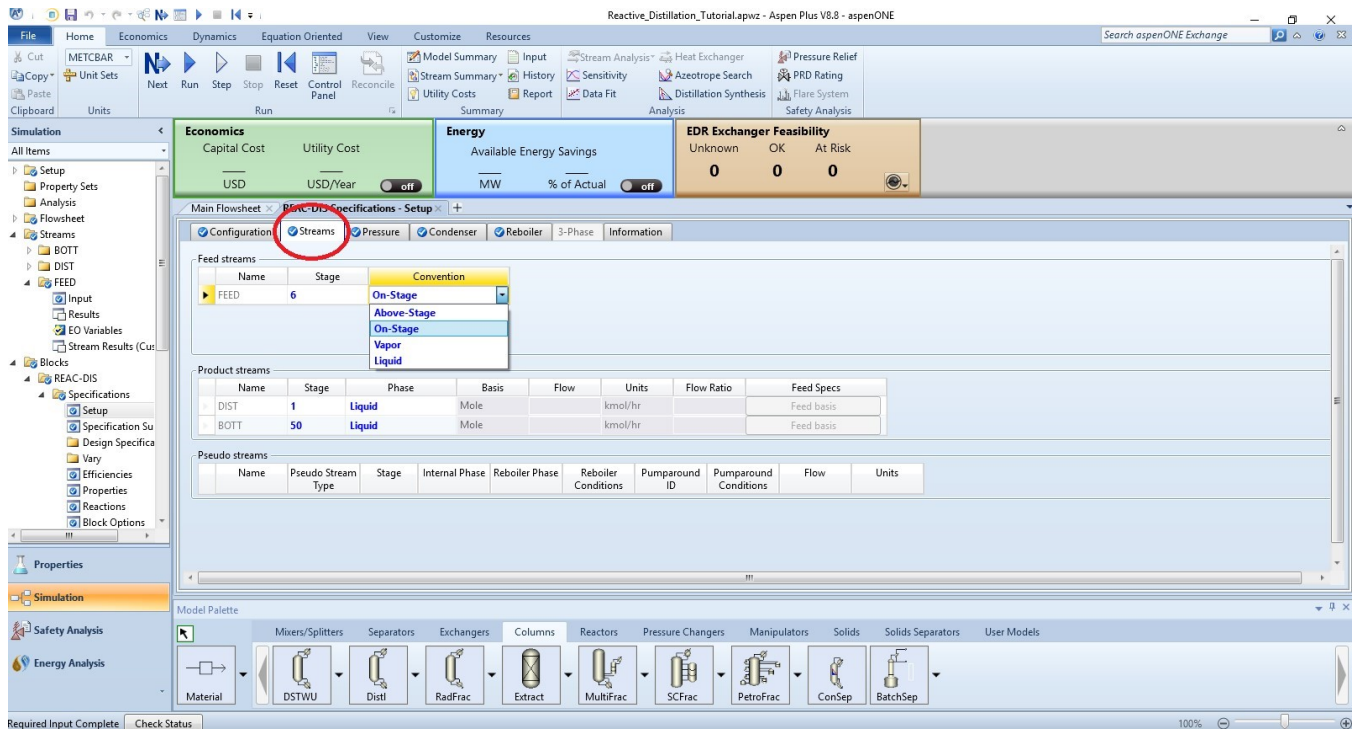
19. Click NEXT or click on the PRESSURE tab, here we specify the column pressure and
    pressure drop (optional). In this example, pressure will be 0.806 MPa with no pressure drop
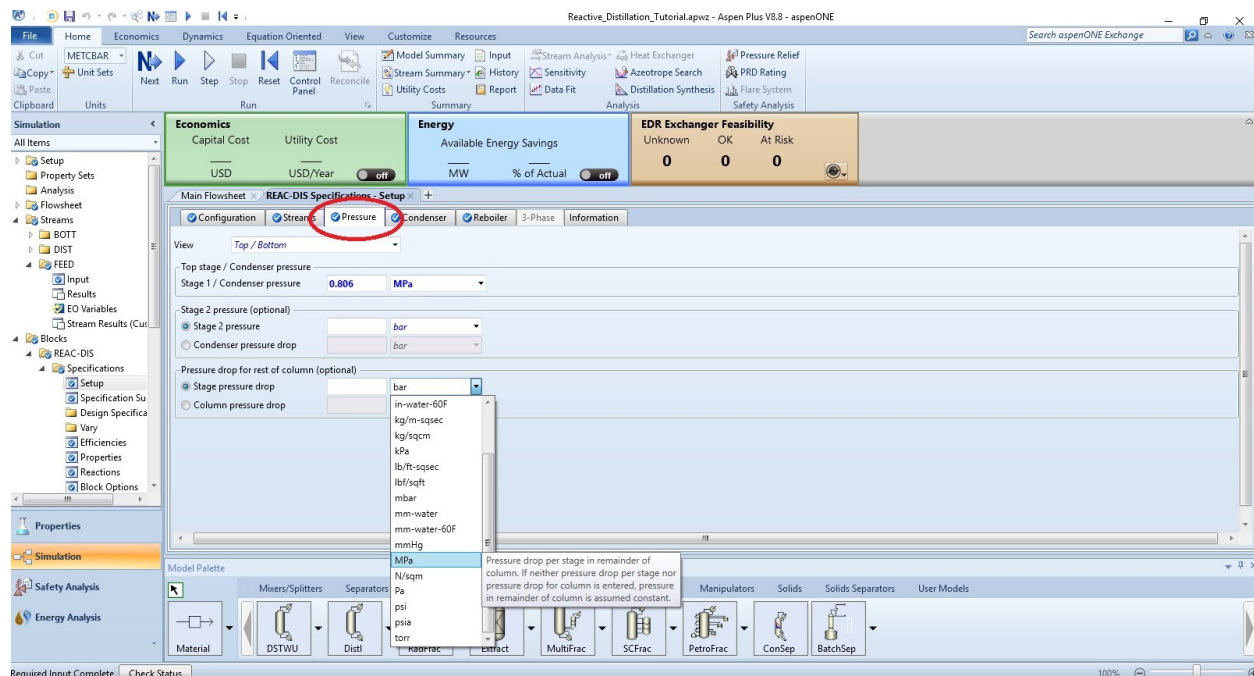
20. Once all the unit specifications are complete go to BLOCKS>REAC-DIS (your process unit name)>SPECIFICATIONS>REACTIONS on the left SIMULATION PANEL. This is where we indicate what stages the catalyst is present on. In this example, the catalyst is present from stages 6-45. Under REACTION-ID in the dropdown menu, select new. A pop-up appears prompting the name of your reaction. Name your reaction (e.g R-1) and click OK.
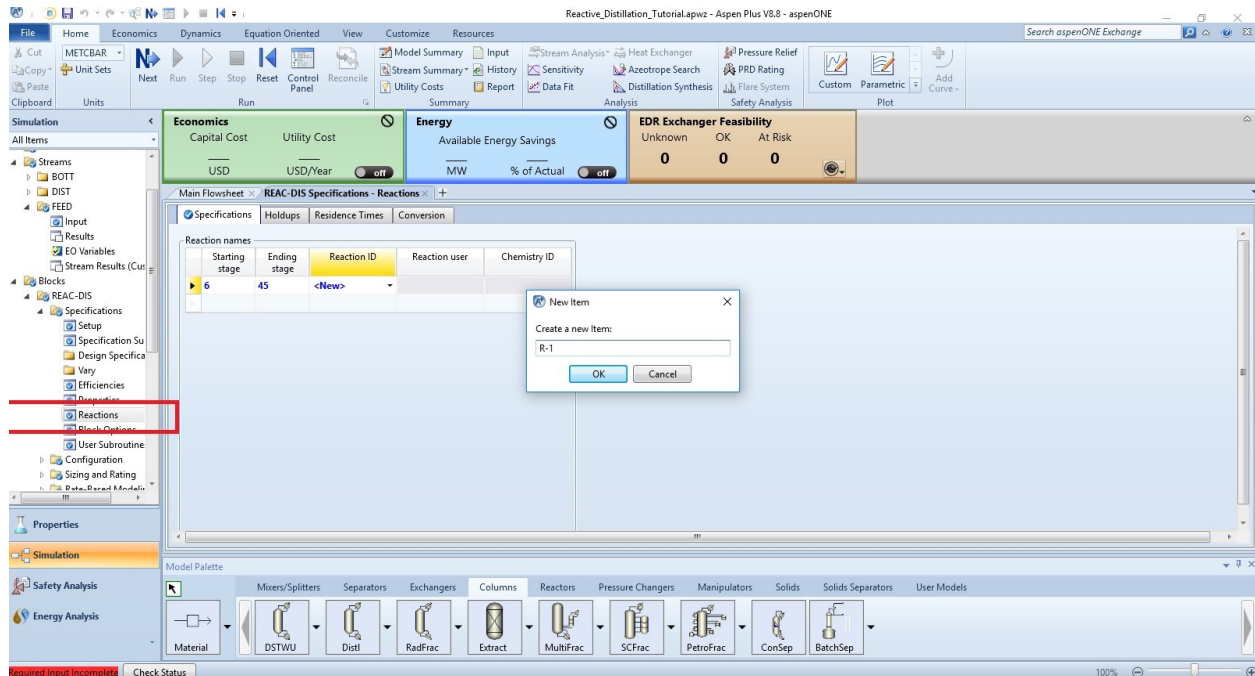
21. In the left SIMULATION PANE, there is a REACTIONS folder (not REACTIONS under the BLOCKS folder) expand it to find your named reaction (R-1 in this case), click on it. Here we create a new reaction type, click the NEW button, a reaction type window will pop-up. Choose KINETIC/EQUILIBRIUM/CONVERSION and click OK.

22. Once you click OK, a reaction editor window will pop-up, here we will choose the reactant components on the left side and reaction product components on the right side along with their reaction coefficients. On the top-right select reaction type as KINETIC. Exponent fields can be left blank if not using Power Law kinetics. **Note**: Reactant coefficients are negative and product coefficients are positive. Once complete, click on the BLUE N (Next) at the bottom of the reaction editor window.
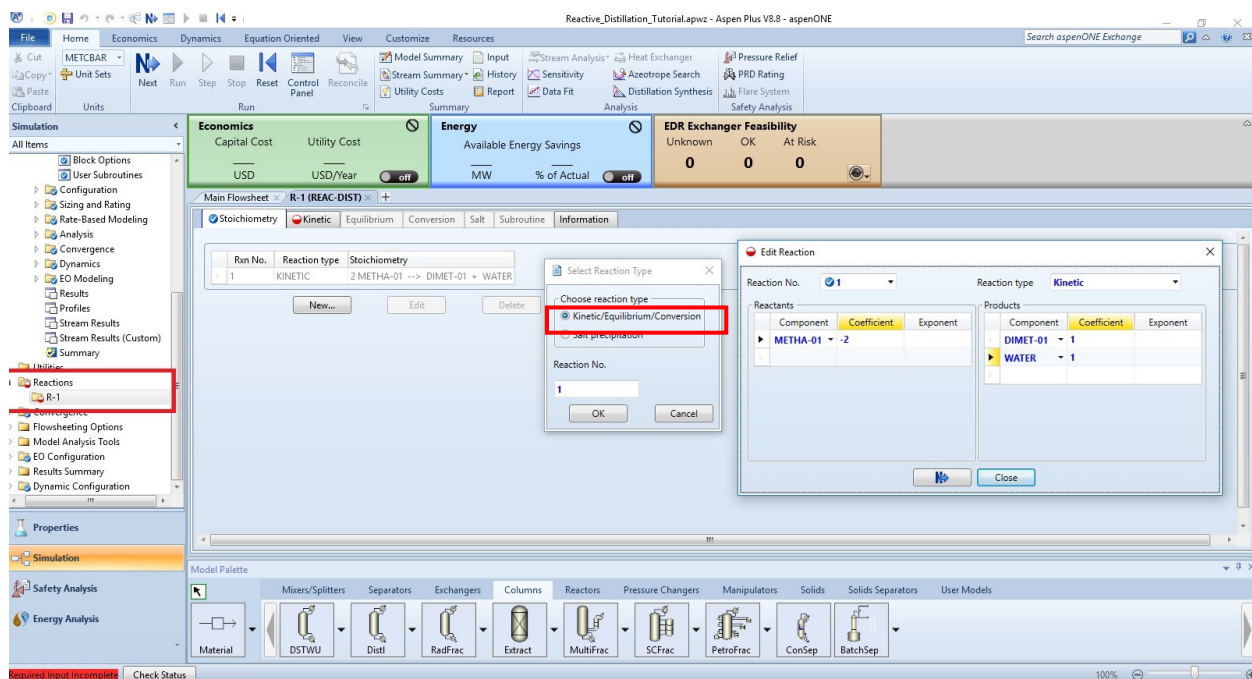
23. Click NEXT, or click the KINETIC tab. In this tab, we will not fill out the required variables but instead select USE USER-KINETIC SUBROUTINE. This will unlock the SUBROUTINE tab.
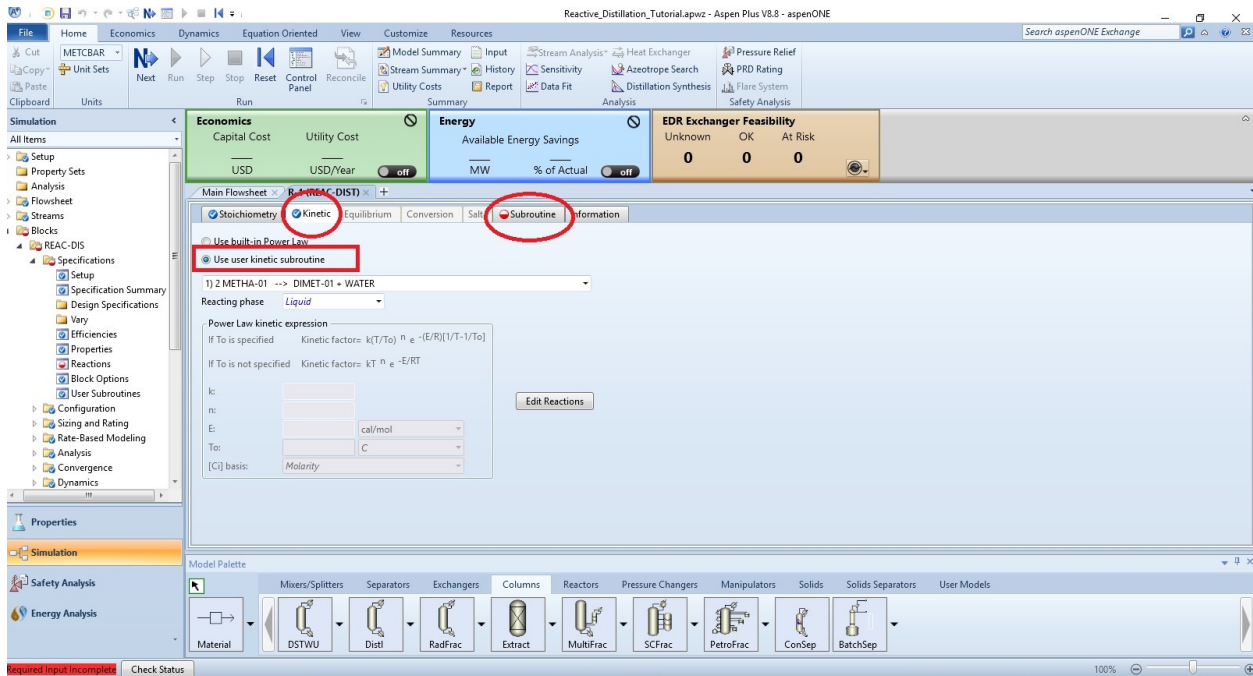
24. Click NEXT, or click the SUBROUTINE tab. Here we will enter the name of our subroutine that we will make. In this example, I named my subroutine "USRKNT." Here you can choose any name for your subroutine but make sure it is no more than six characters and without symbols.
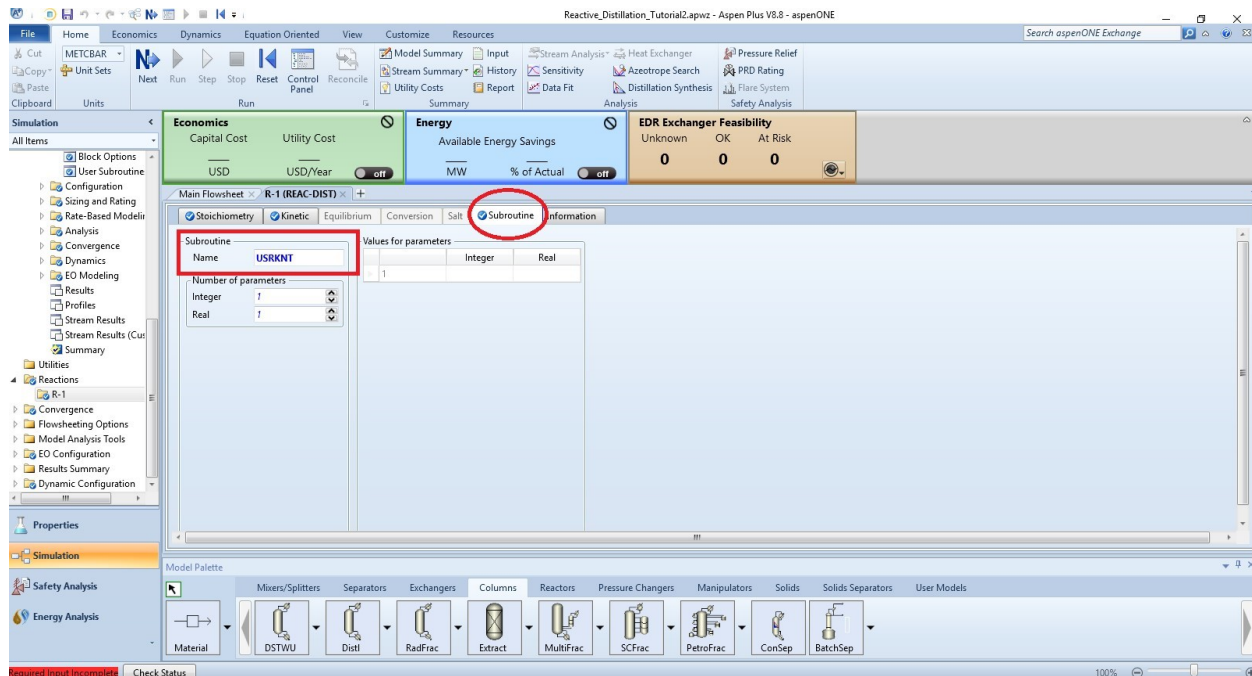
25. Click on NEXT, or manually return to BLOCKS>REAC-DIS (your process unit name)>SPECIFICATIONS>REACTIONS on the left SIMULATION PANEL. Once there, you will notice the HOLDUPS tab has a half red circle (this means incomplete, input is required for this field). Click on the HOLDUPS tab, here we are required to enter on which the stages the catalyst is present and the liquid holdup. The liquid holdup here represents the amount of catalyst that is present in the column. For this example, like step 20 the catalyst will be present from stage 6 to 45 at a catalyst holdup of 900 kg.
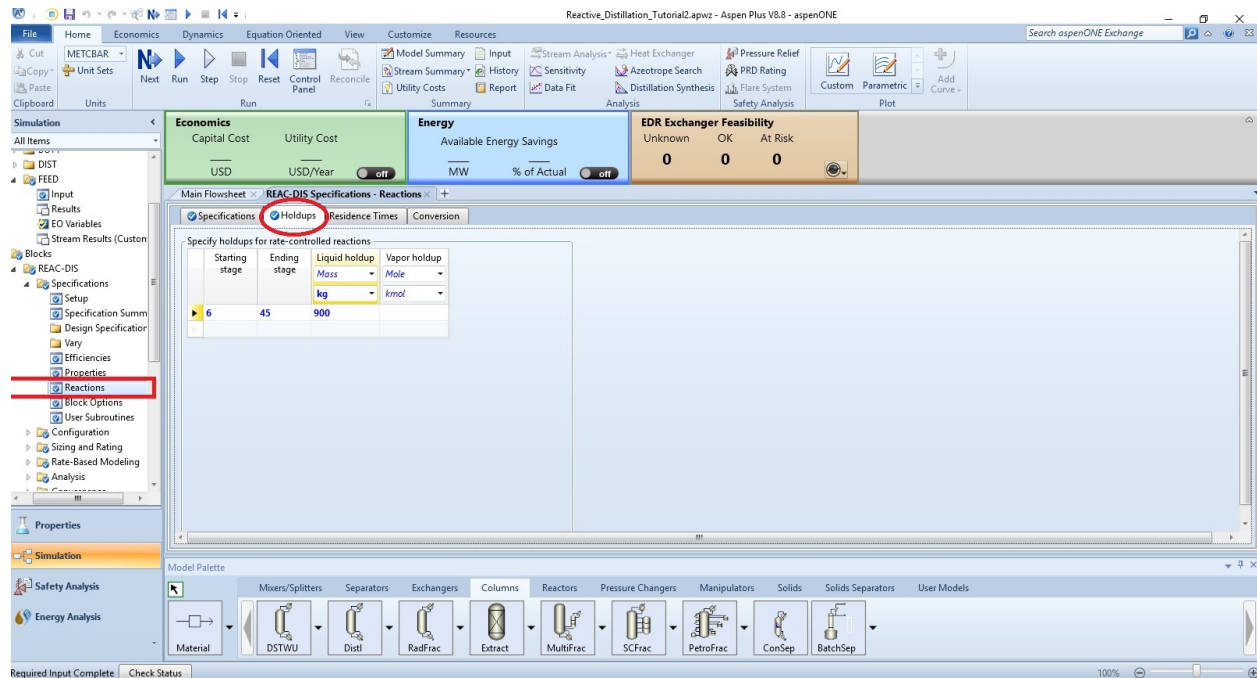
26. If you click NEXT at this point, a pop-up will appear saying all required inputs are complete. If Aspen Plus takes you to another tab, make sure to complete all the inputs it is prompting you to complete. The pop-up will ask you to "Run the simulation now?" Click CANCEL, we still need to produce and link the kinetic subroutine to simulation.
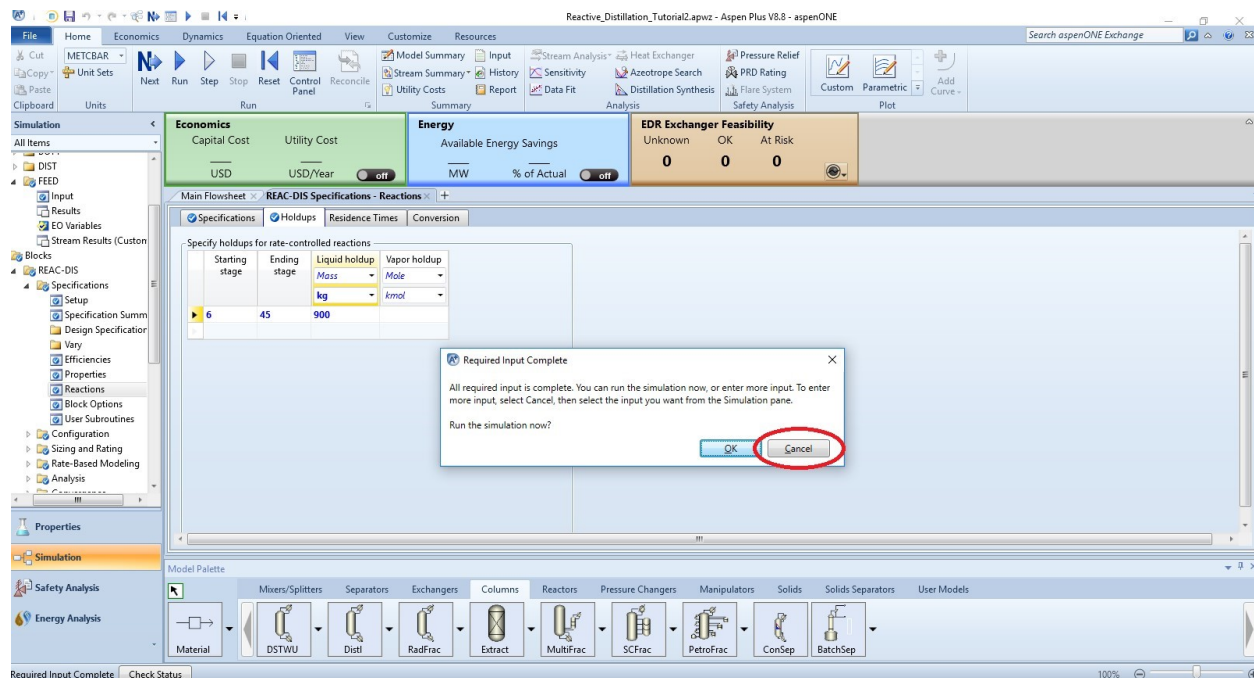
Producing the Kinetic Subroutine

27. First minimize Aspen Plus, then go to START

MENU>PROGRAMS>ASPENTECH>PROCESS MODELING (version #, V8.8 in this

example)>ASPEN PLUS> SELECT COMPILER FOR ASPEN PLUS. The location may be

different for other users, for me the COMPILER SETTINGS were in START MENU>

PROGRAMS> ASPEN PROPERTIES V8.8> SELECT COMPILER FOR ASPEN PLUS.

Once you double click the SELECT COMPILER a black pop-up window will appear with a

list of different versions of intel Fortran compiler programs and corresponding editors. You

will have to download one Intel Fortran program and its corresponding editor on the list. For

example, if you download Intel Fortran Version 2013SP1 and Microsoft Visual Studio

V2013 which is option 37 on the table it will change its STATE from ERROR to OK. Once

you're able to download the correct combination at the bottom it will prompt you to enter an

option from 1 to 41. Since option 37 is the combination open, I will type in "37."
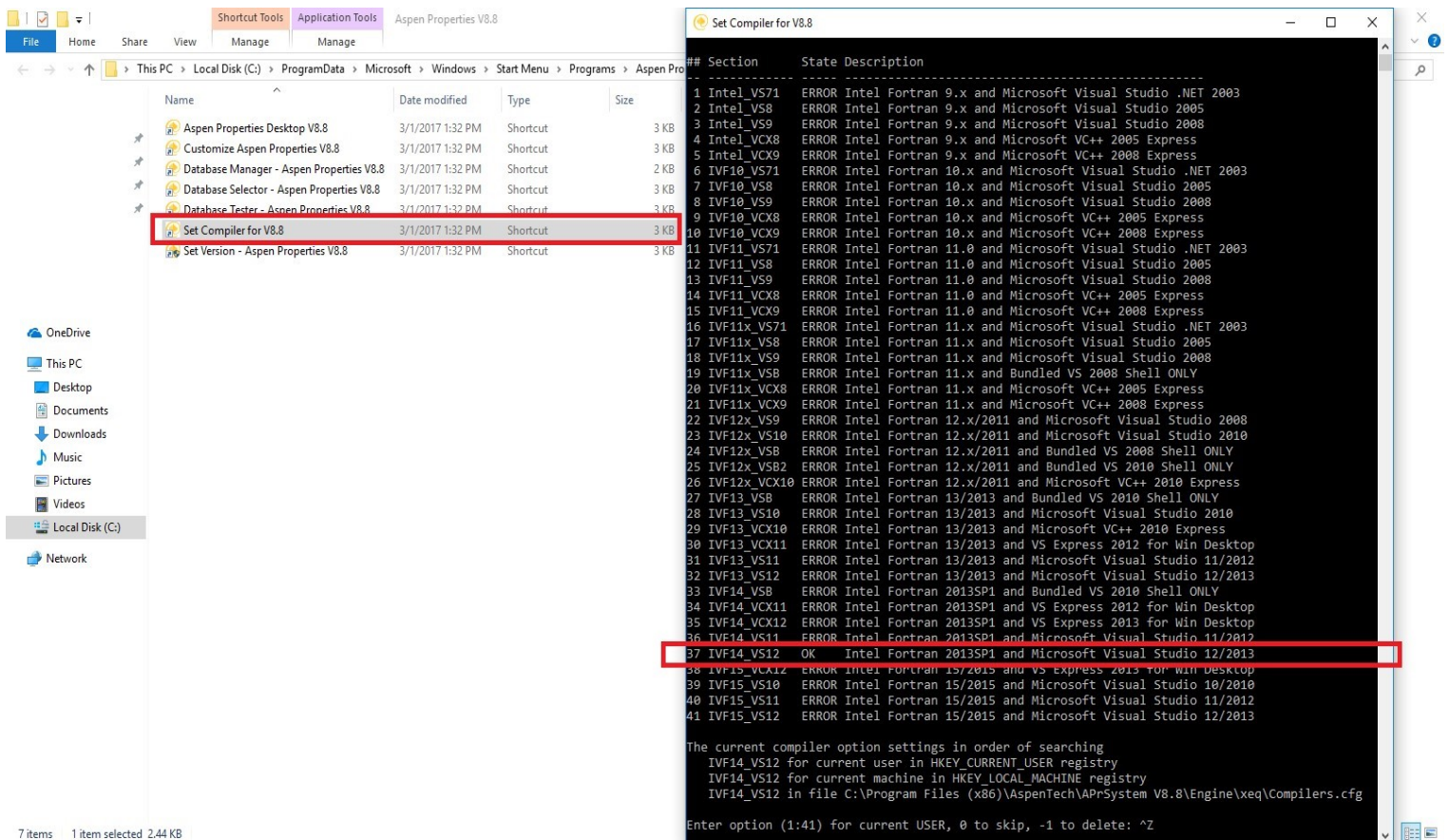
28. Once the compiler and editor are set, go to LOCAL DISK (C:)>PROGRAM

FILES(x86)>ASPENTECH> ASPEN PLUS V8.8> ENGINE> USER. Here you will see a

list of numerous subroutine examples for different user models. **Note**: The location of user

model examples may not follow the same path for each user. You will have to search for the

user folder. In the folder open the subroutine for reactive distillation called "usrknt" using the

editor program you downloaded in step 27. The Fortran code below is what you will see with

a lot of added comments. As you can see on line 16 after subroutine it says "USRKNT." if

the name of your subroutine in step 24 was different, please make the change here to the one

of your subroutine name in Aspen PLUS. If you were unsuccessful in finding the user model

library by Aspen Plus, copy the code below into a blank Fortran editor (without the line numbers).

```
1.          C $Log: usrknt.f,v $
2.          C Revision 1.3  1996/05/21  19:25:07  apbuild
3.          C ANAVI 9.3 upgrade
4.          C
5.          C Revision 1.2  1996/04/26  19:15:09  apbuild
6.          C Introduce 3phase modifications, Venkat
7.          C
8.          C ==========================cvs revision
            history=========================
9.          C$ #3 BY: SIVA DATE: 15-NOV-1994 ADD DOCUMENTATION
10.         C$ #2 BY: SIVA DATE: 21-JUL-1994 ADD X TO ARGUMENT LIST
11.         C$ #1 BY: ANAVI DATE:  1-JUL-1994 NEW FOR USER MODELS
12.         C
13.         C     User Kinetics Subroutine for RADFRAC, BATCHFRAC, RATEFRAC
14.         C     (REAC-DIST type Reactions)
15.         C
16.         SUBROUTINE USRKNT (N,      NCOMP,  NR,     NRL,     NRV,
17.         2                  T,      TLIQ,   TVAP,   P,      PHFRAC, 18.
            3                  F,      X,      Y,      IDX,     NBOPST,
19.         4                  KDIAG,  STOIC,  IHLBAS, HLDLIQ,  TIMLIQ,
20.         5                  IHVBAS, HLDVAP, TIMVAP, NINT,    INT,
21.         6                  NREAL,  REAL,   RATES,  RATEL,   RATEV,
22.         7                  NINTB,  INTB,   NREALB, REALB,   NIWORK,
23.         8                  IWORK,  NWORK,  WORK)
24.         IMPLICIT NONE
25.         C
26.         C     DECLARE VARIABLES USED IN DIMENSIONING
27.         C
28.         INTEGER NCOMP, NR,   NRV,  NINT, NINTB,
29.         +       NREALB,NIWORK,NWORK
30.         C
31.         #include "ppexec_user.cmn"
32.         EQUIVALENCE (RMISS, USER_RUMISS)
33.         EQUIVALENCE (IMISS, USER_IUMISS)
34.         C***************************************************************
            *** 35. C     DECLARE ARGUMENTS
36.         C
37.         INTEGER NRL(3),IDX(NCOMP),   NBOPST(6),
38.         +       INT(NINT),    INTB(NINTB),
39.         +       IWORK(NIWORK),N,      KDIAG, IHLBAS,
40.         +       IHVBAS,NREAL
41.         REAL*8 PHFRAC(3),    X(NCOMP,3),   Y(NCOMP),
42.         +       STOIC(NCOMP,NR),     RATES(NCOMP),
43.         +       RATEL(1),     RATEV(NRV),
44.         +       REALB(NREALB),WORK(NWORK), T,     TLIQ,
45.         +       TVAP, P,    F,     HLDLIQ,TIMLIQ
46.         REAL*8 HLDVAP,TIMVAP
47.         C
48.         C     DECLARE LOCAL VARIABLES
49.         C
50.         INTEGER IMISS
51.         REAL*8 REAL(NREAL),  RMISS
52.         C
53.         C     BEGIN EXECUTABLE CODE
```

```
54.        C
55.        RETURN
56.        END
```

29. Under line 52 you will see "BEGIN EXECUTABLE CODE," below this line you should

    write the kinetics of your reaction. In this example, the kinetics are in Langmuir-

    Hinshelwood-Hougen-Watson form as shown below.

$$r_{DME} = \frac{k_S \, C_M^2}{\left(C_M + \frac{K_W}{K_M} C_W \right)^2}$$

$$k_S = 6.12 \times 10^7 \, \frac{mol}{kg \cdot cat \cdot s} \, \exp(-\frac{98,000 \, J/mol}{RT})$$

$$\frac{K_W}{K_M} = \exp(-6.46 + \frac{2964}{T})$$

The following code was added into the subroutine for kinetics of the reaction:

```
REAL*8 Cm, Cw, RATE, Kw, Ks
Cm = 13*X(2,3)
Cw = 13*X(1,3)
Ks = 61200000*EXP(-98000.0/(8.314*T))
Kw = EXP(-6.46+2964.0/T)
RATE = HLDLIQ*Ks*Cm*Cm/((Kw*Cw+Cm)*(Kw*Cw+Cm))
RATES(1) = RATE
RATES(3) = RATE
RATES(2) = -
2*RATE
```

NOTE: the numbers in the parentheses for RATES(#) and X(#,3) in the above code corresponds

to the order of components added in step 5

30. Once your code is complete, save it in an empty folder. I recommend saving the code

    filename the same as your subroutine name ("usrknt" in this case). DO NOT FORGET to put

.f or **.for** at the end of your filename to specify that the code is in Fortran (e.g usrknt.f or usrknt.for)

Similar to step 27 go to START MENU> PROGRAMS> ASPENTECH> PROCESS MODELING (version #, V8.8 in this example)> ASPEN PLUS. The location may be different for other users, for me the COMPILER SETTINGS were in START MENU> PROGRAMS> ASPEN PLUS V8.8> CUSTOMIZE ASPEN PLUS V8.8. Once you double click CUSTOMIZE ASPEN PLUS V8.8 (Simulation Engine Window) a black pop-up window will appear. The first thing we want to do is change the directory of the engine window to the folder we saved our Fortran subroutine code. In my case I saved the Fortran file in "C:\UserModels" so I will type into the engine "cd C:\UserModels". You will notice the directory change. Now we will compile the Fortran code by typing "aspcomp name_of_your_fortran_file.f" in this case I will type "aspcomp usrknt.f". If there is a mistake in the code you will get an error message during compiling with line numbers of the errors present in the code. Return to the code and fix the errors and compile again. If the code was successfully compiled you will see no message in the simulation engine, and an object file under the same file name appear in the folder. Now open notepad and type in the directory of the object file that was just created and save the file as an **.opt** file. This will direct Aspen Plus to the Fortran file that it needs to read.
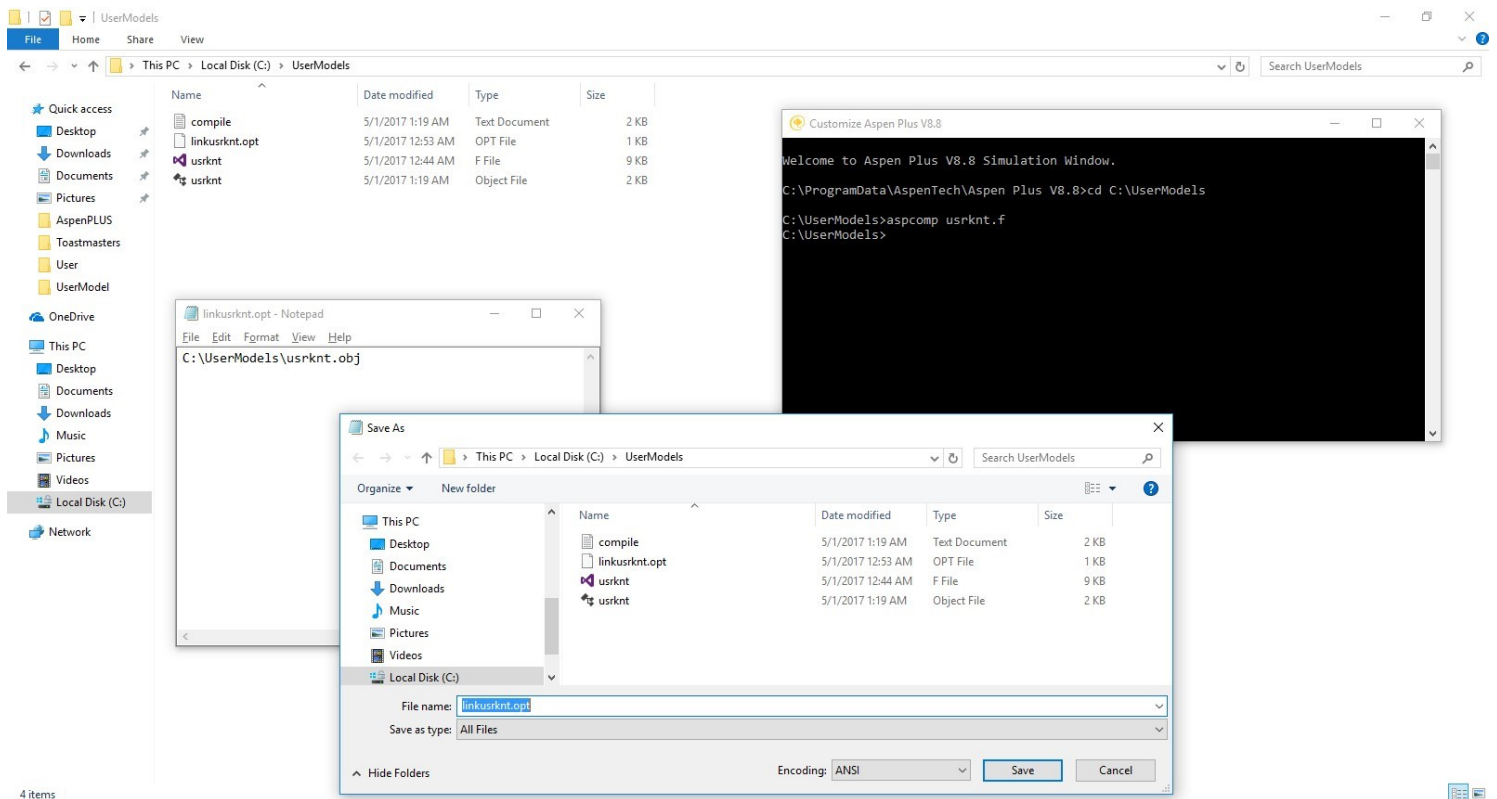
32. Now we are required to link the **.opt** file to Aspen Plus. To do this, type "asplink [dlopt name_of_the_opt_file_you_created.opt] name_of_your_fortran_file". In this case, I will type "asplink [dlopt linkusrknt.opt] usrknt" and press ENTER. You should get a message saying:

    Linking usrknt.dll; sending messages to usrknt.ld

    usrknt.dll created.

This will create multiple files, including a **.dll** file with the same name as your Fortran file. Open notepad and type in the directory of the **.dll** file that was just created and save the file as an **.opt** file.
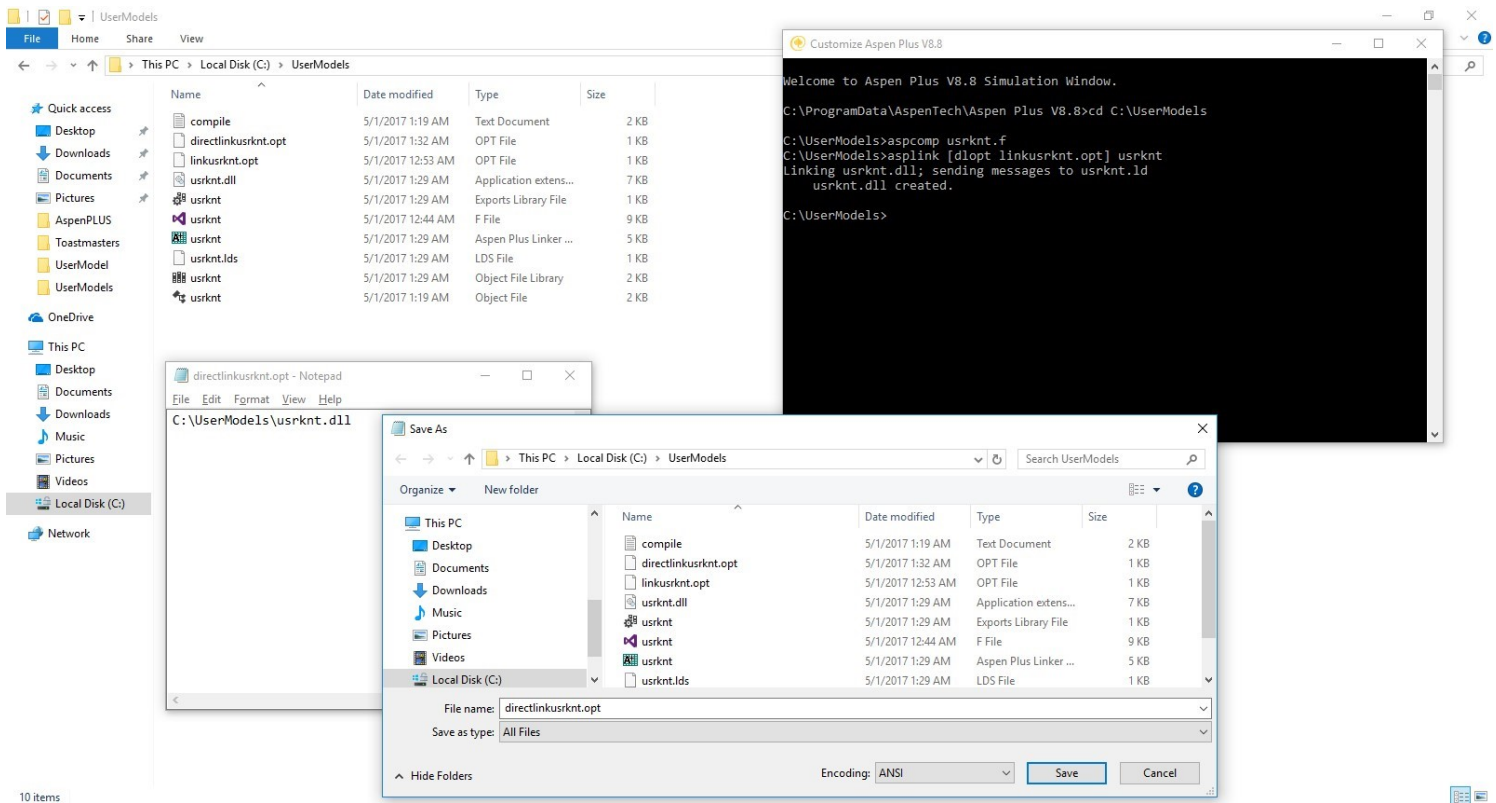
33. Now return to the Aspen Plus simulation, open RUN SETTINGS by clicking on the small
box on the HOME toolbar in the bottom right corner of the RUN section. Under
MISCELLANEOUS FILES in the LINKER OPTIONS type in the directory of the **.opt**
recently created that includes the directory of the **.dll** file. Since the name of my **.opt** file is
"directlinkusrknt.opt" I will type "C:\UserModels\directlinkusrknt.opt" press APPLY and
click OK. Now the simulation can finally be started. On the top HOME toolbar in the RUN
section, click RUN.
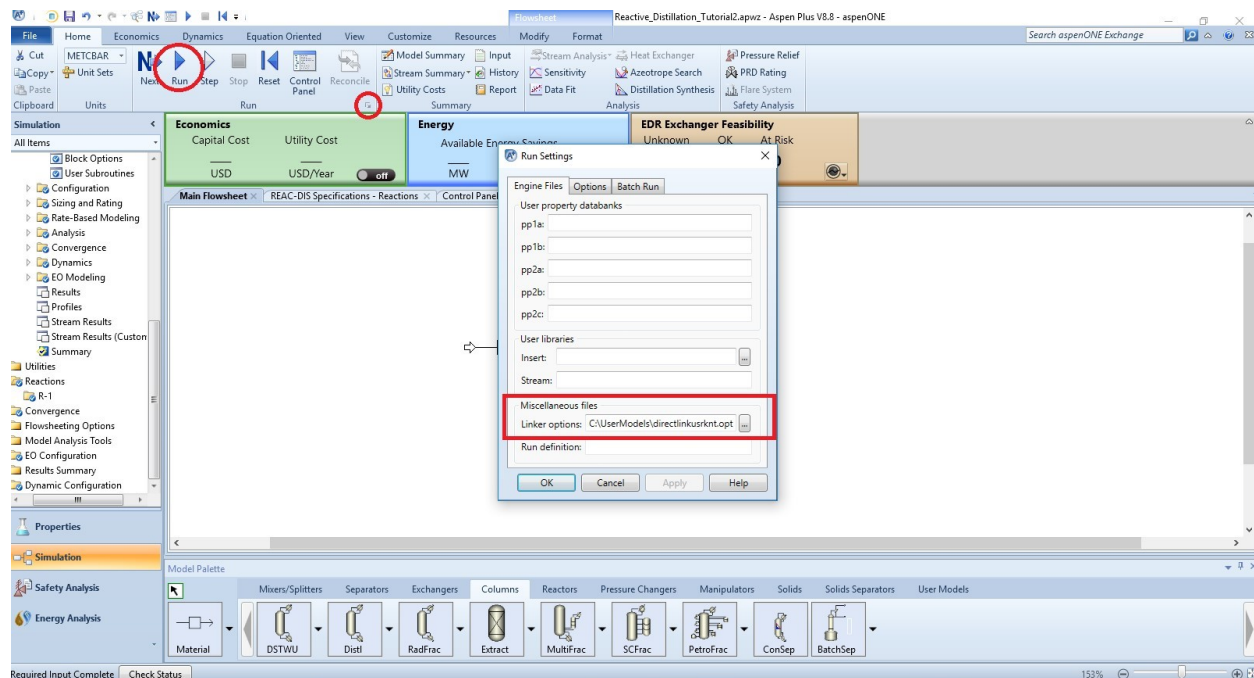
34. Once the simulation is complete you will see RESULTS AVAILABLE on the bottom left

    corner of the simulation screen. Under the HOME toolbar, in the RUN SECTION click on

    the icon CONTROL PANEL. This will give us a summary of the simulation convergence, its

    iterations, tolerance, error, and any warnings or errors that may have arisen during

    calculations. If your simulation completed with errors or warnings, read the warning/error

    messages in the CONTROL PANEL and adjust your simulation appropriately. Aspen Plus

    begins its convergence calculations from the last convergence point, therefore if you change

    your simulation it is best to press the RESET button beside the RUN button to reinitialize the

    simulation and start convergence calculations from zero rather than the last point.
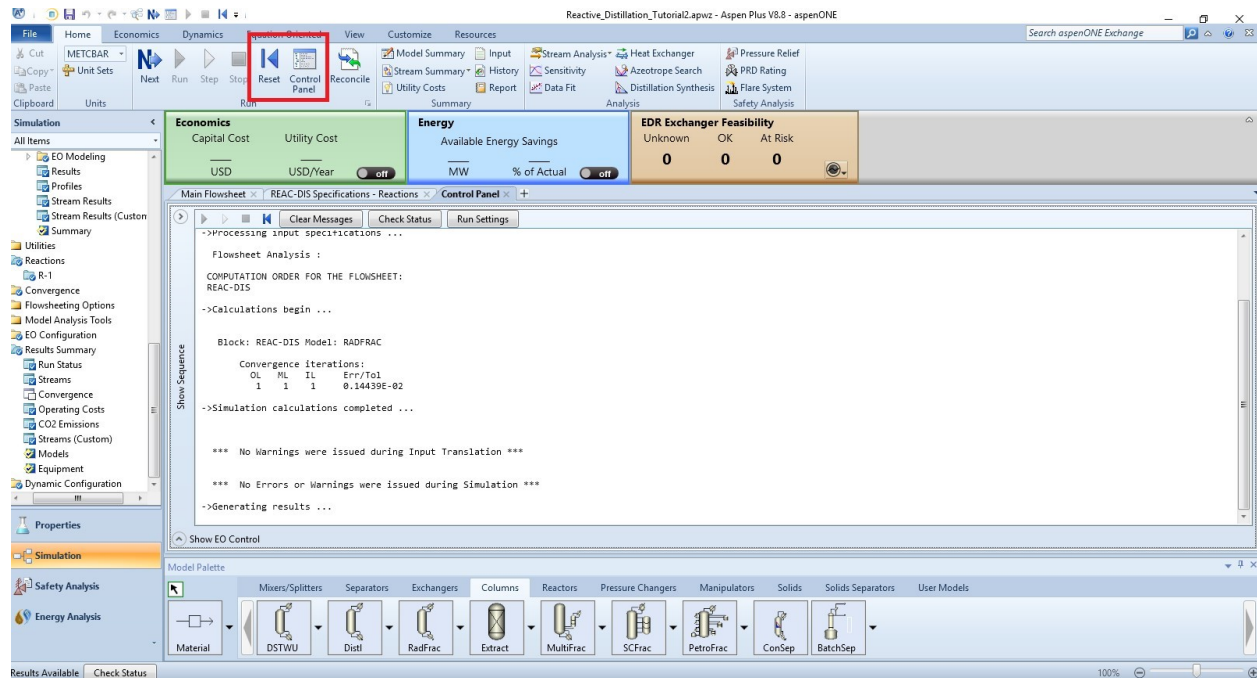
35. Now to see your results, go to the RESULTS SUMMARY folder in the SIMULATION

PANEL window to the left and click on STREAMS (CUSTOM). Here will be a table of

streams and their corresponding information. You can add streams at the top of the table

through a dropdown menu.
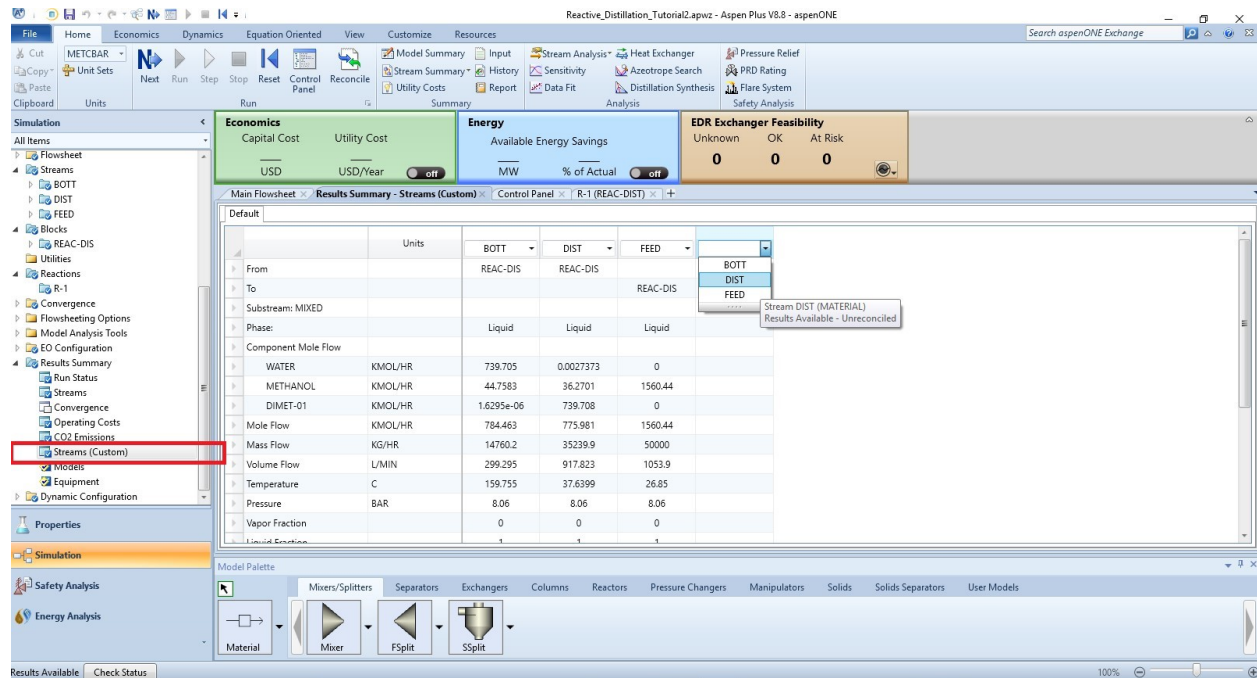
36. If some of the information about the streams is not present you can toggle the information

shown by going to the SETUP folder in the SIMULATION PANEL on the left and click

REPORT OPTIONS, go to the STREAMS tab and check off all the items to be included in

your stream reports.
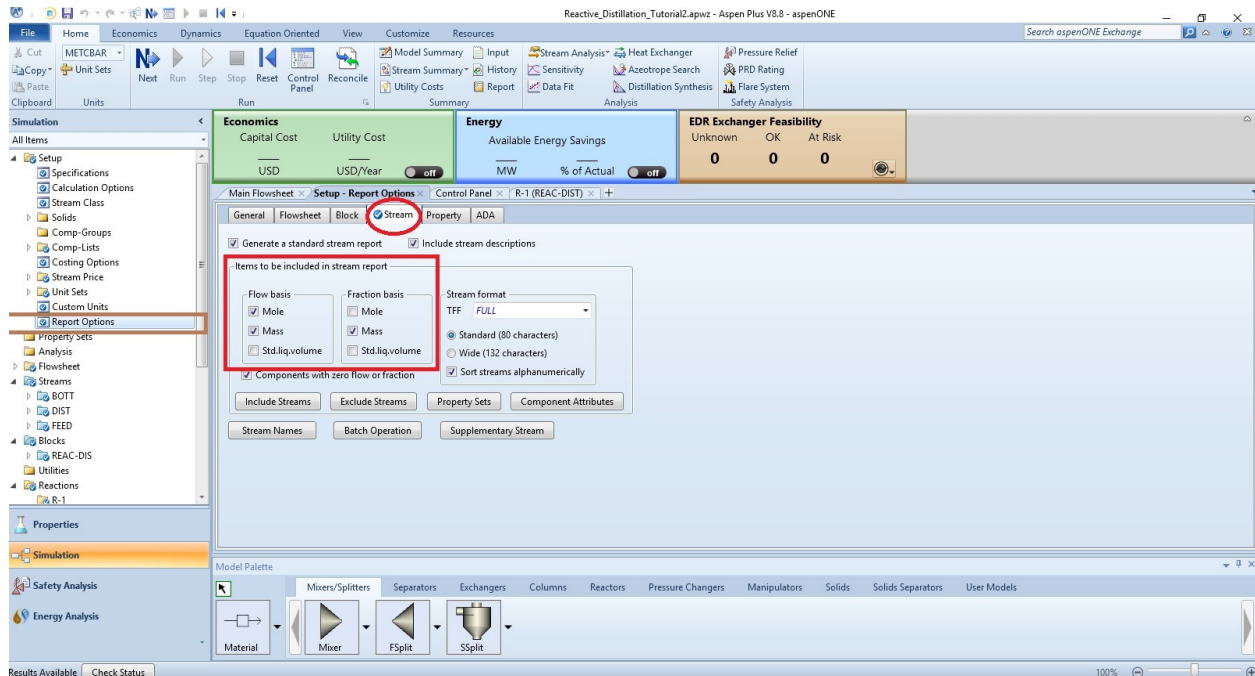
37. Go back to STREAMS (CUSTOM) and press PLAY once again to see the new stream

    report.
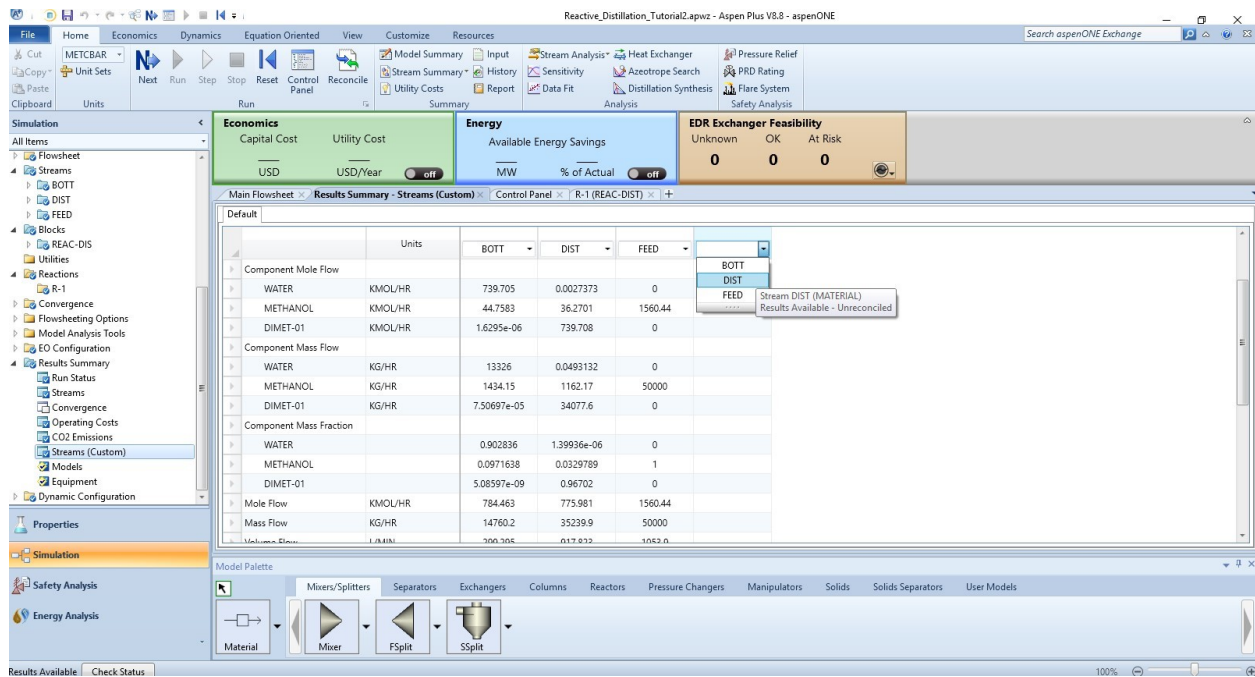
Sensitivity Analysis

- We will perform a sensitivity analysis of the reactive distillation and the effect of different reflux ratios on the purity of DME in the top product

38. Go to MODEL ANALYSIS TOOLS folder on the left side in the SIMULATION panel and click SENSITIVITY. Click the NEW button and a pop-up window will appear asking to enter your sensitivity ID name (S-3 in this case), then click the OK button.
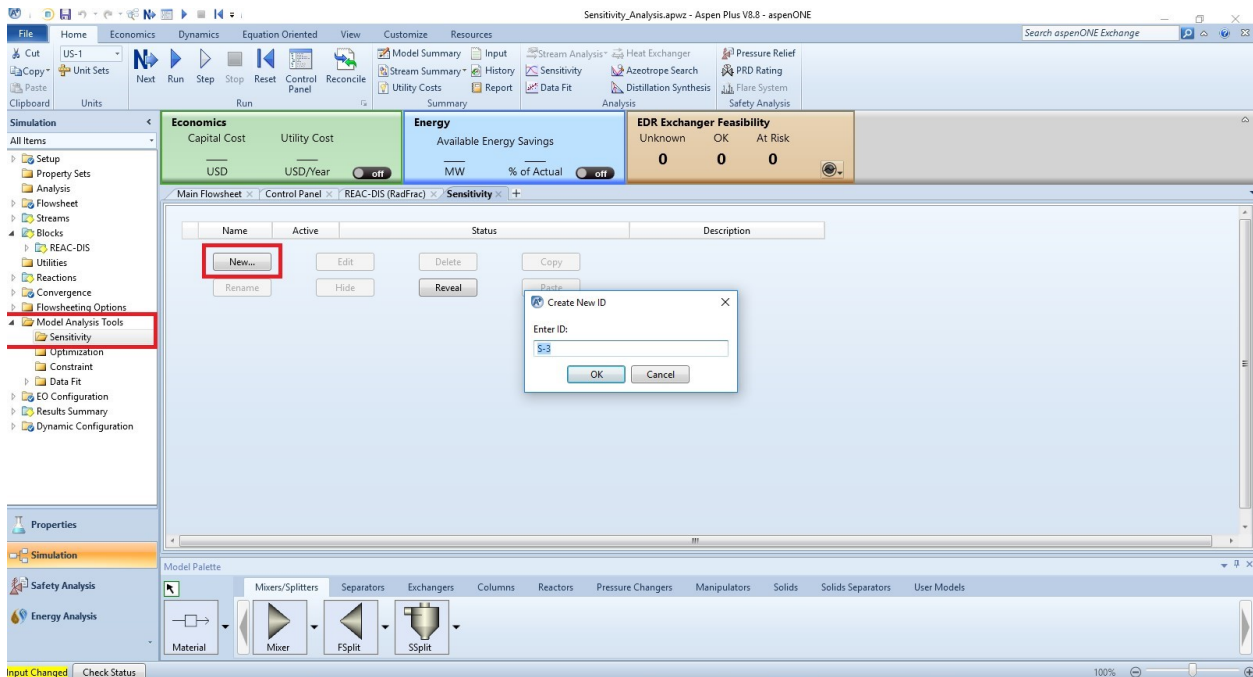
39. In the first tab of the sensitivity analysis which is "VARY", we need to specify the variable that we would like to vary to determine its effect on the variable of choice. In this case, we would like to vary the column reflux ratio. Click NEW, go to the TYPE dropdown menu and select BLOCK VARIABLE, this specifies that the variable of change is a block variable, the block being the reactive distillation column. Next in the BLOCK dropdown menu that

appears choose REAC-DIS (the given name of your column). In the VARIABLE dropdown

menu that appears choose MASS-RR which represents the varied component as the mass

reflux ratio. In the LOWER and UPPER sections, specify the upper and lower limits of your

sensitivity analysis (In this example, we will choose a reflux ratio from 2 to 10), Choose

between NUMBER OF POINTS or INCREMENTS for number of data points (In this case,

INCREMENT = 1).
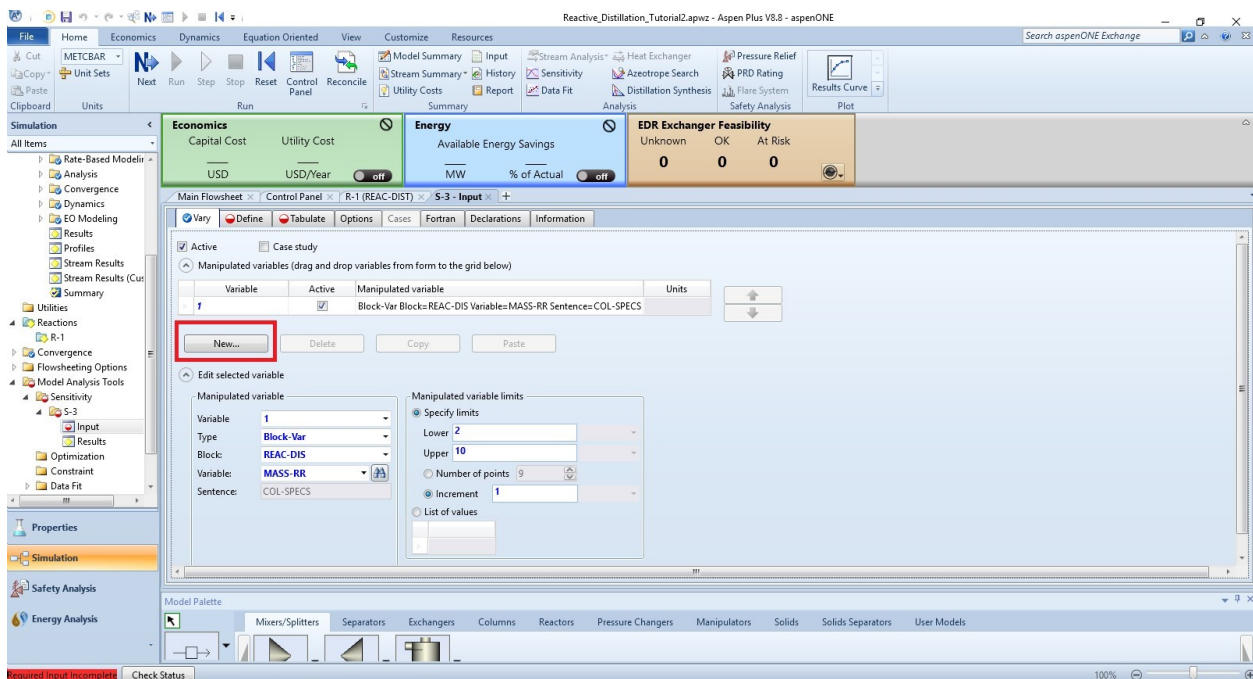
40. Once all the input is complete a blue circle will appear in the VARY tab. Go to the DEFINE

tab or click NEXT. Here we will define the variables we would like to measure during the

sensitivity analysis, which in this case is the mole fraction of DME in the distillate. Click

NEW, enter the variable name (e.g DME) and click OK. Then select STREAMS because the

variable is a STREAMS variable. In the TYPE dropdown menu choose MOLE-FRAC. In the

STREAMS dropdown menu that appears choose DIST (the name given to your top stream)

because the mole fraction we want is in the distillate. In the COMPONENT dropdown menu

that appears choose DIMET-01 which is the dimethyl ether component.
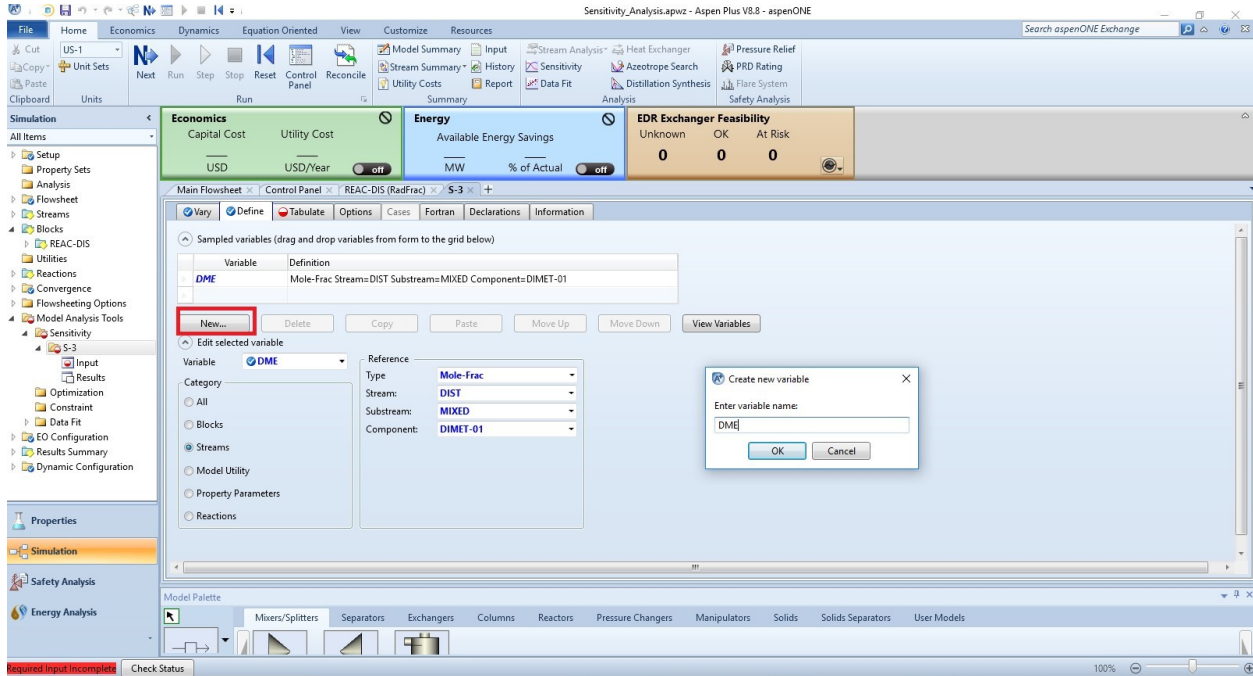
41. Once all the input is complete a blue circle will appear in the DEFINE tab. Go to the

TABULATE tab or click NEXT. Click the FILL VARIABLES button and click RUN.
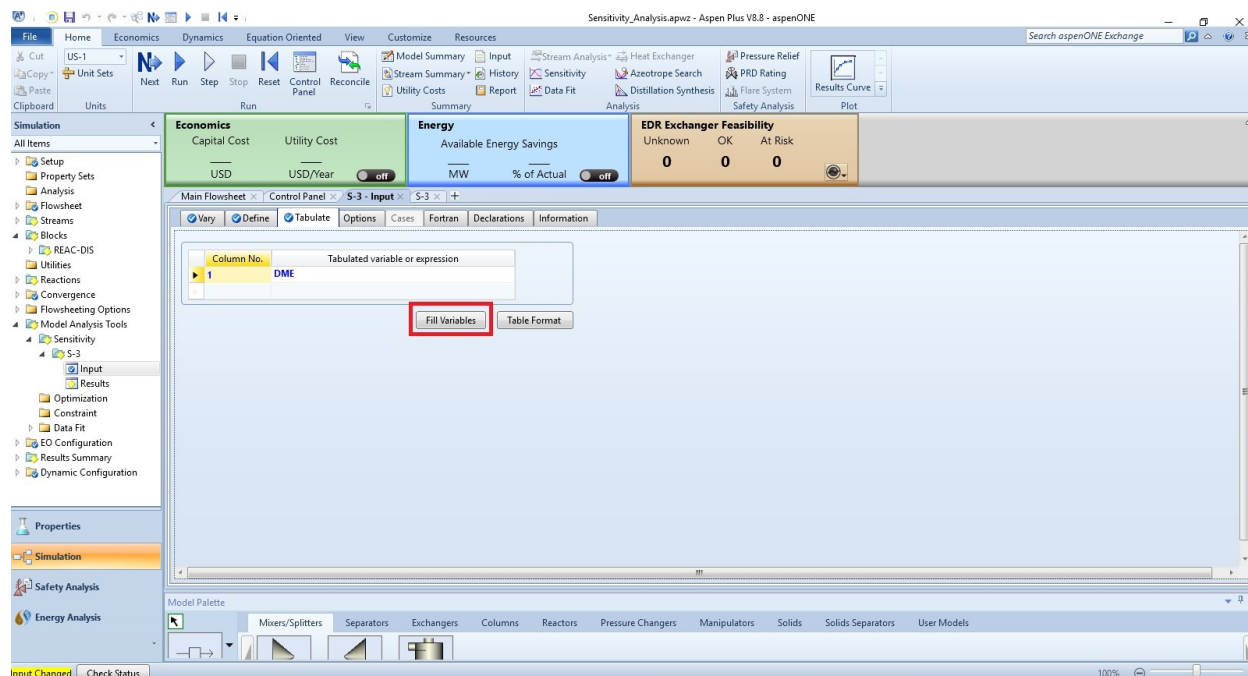
42. If the simulation was completed successfully go to SENSITIVITY>S-3 (name of your sensitivity analysis)>RESULTS and a table with all the mole fractions of DME at different reflux rations will be shown in a table. These results can be copied into excel for plotting. Under the STATUS column all rows should state OK, if a value states ERROR then that row value is INCORRECT and is only the copied previous row values. Check the control panel (accessed by clicking the CONTROL PANEL button above the RUN section in the HOME toolbar) for error messages and adjust your simulation appropriately.
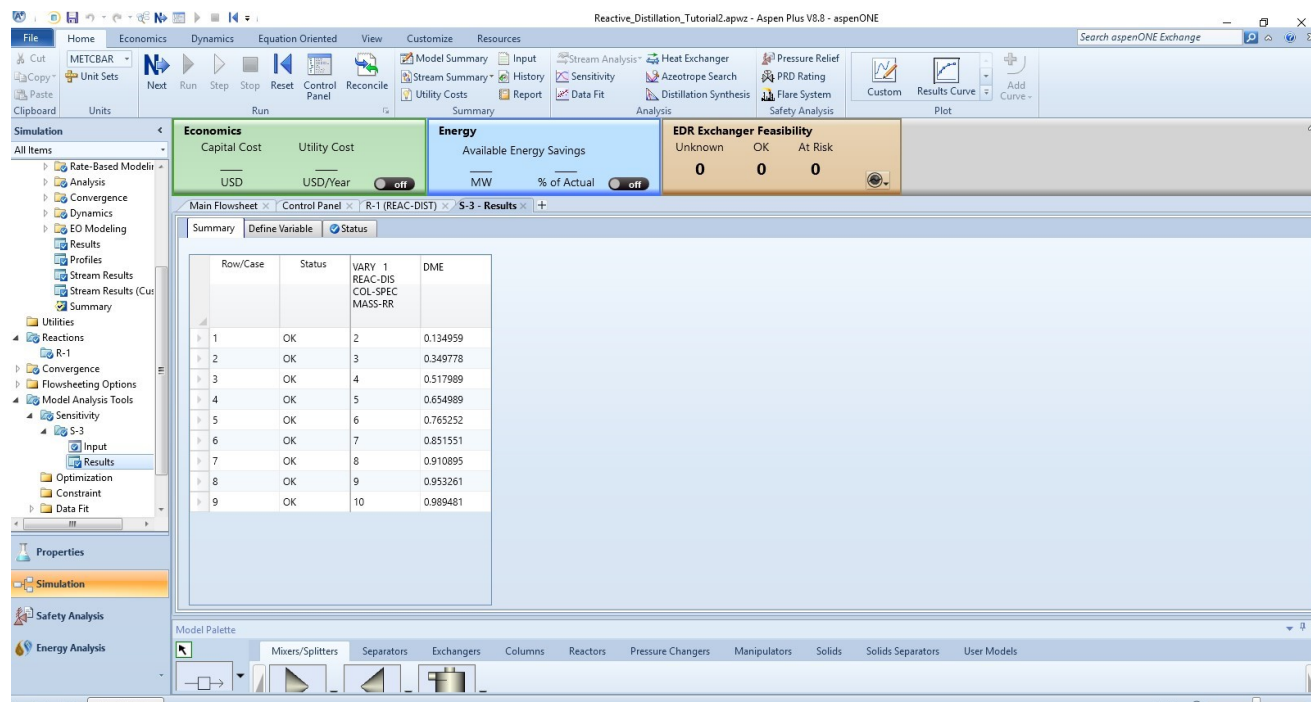
43. If you would like a visual of your sensitivity results, click RESULTS CURVE in the HOME

toolbar above the PLOT section. A pop-up will appear asking for the X-AXIS variable and

the VARIABLE CURVES to plot, choose MOLE-RR from the dropdown menu as the x-axis

and check mark DME. Press OK and the sensitivity curve will appear. All formatting of the

plot can be done through the FORMAT tab in the toolbar.
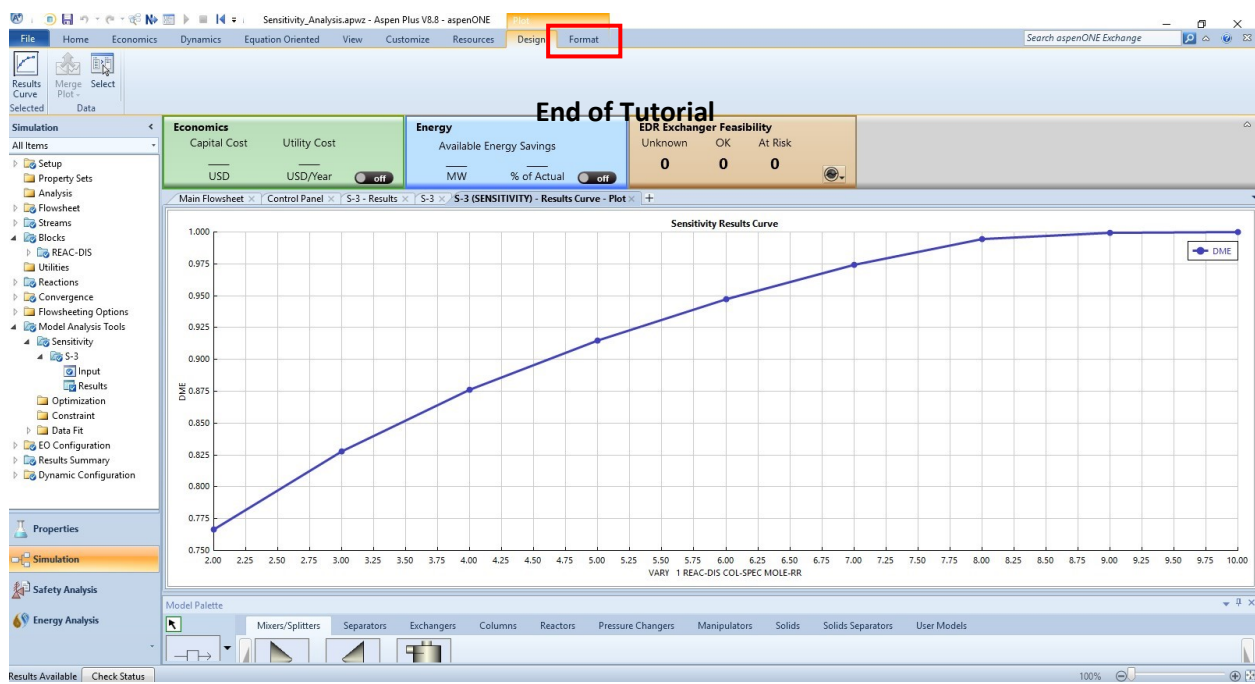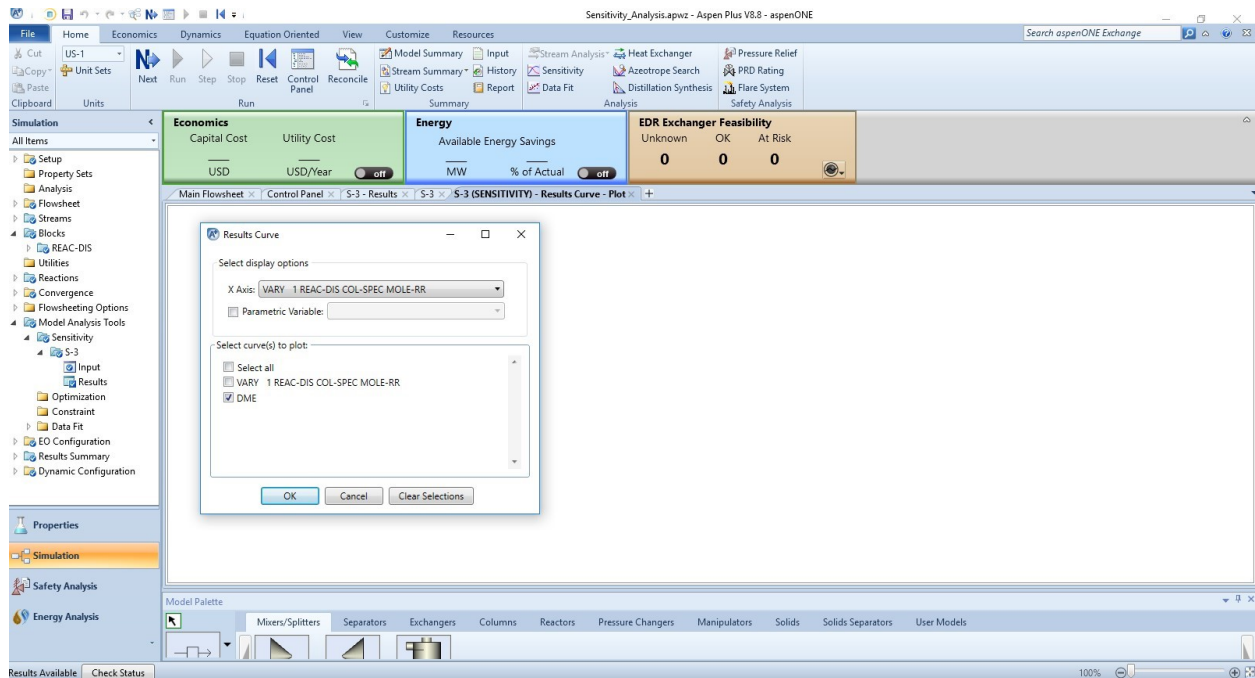
44. Sensitivity analysis can be repeated for many different variables

End of Tutorial

Appendix B: Aspen Plus Input and Output Report

```
DYNAMICS
    DYNAMICS RESULTS=ON

IN-UNITS SI FLOW='kg/hr' MASS-FLOW='kg/hr' MOLE-FLOW='mol/hr'  &
        PRESSURE=MPa PDROP='N/sqm'

DEF-STREAMS CONVEN ALL

MODEL-OPTION

DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
        'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD

PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' &
        / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'

COMPONENTS
    DIMET-01 C2H6O-1 /
    METHA-01 CH4O /
    WATER H2O

SOLVE
    RUN-MODE MODE=SIM

FLOWSHEET
    BLOCK REAC-DIS IN=FEED OUT=DIST BOTT

PROPERTIES NRTL
    PROPERTIES NRTL-SAC

ESTIMATE ALL
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
    NRTL ALL ALL UNIFAC

PROP-DATA NRTL-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
    PROP-LIST NRTL
    BPVAL DIMET-01 METHA-01 0.0 -18.93720000 .2951000000 0.0  &
        0.0 0.0 0.0 0.0
    BPVAL METHA-01 DIMET-01 0.0 653.0063000 .2951000000 0.0  &
        0.0 0.0 0.0 0.0
    BPVAL METHA-01 WATER -.6930000000 172.9871000 .3000000000  &
        0.0 0.0 0.0 24.99000000 100.0000000
    BPVAL WATER METHA-01 2.732200000 -617.2687000 .3000000000  &
        0.0 0.0 0.0 24.99000000 100.0000000
    BPVAL DIMET-01 WATER 0.0 -139.3800180 .3000000000 0.0 0.0  &
        0.0 25.00000000 25.00000000
    BPVAL WATER DIMET-01 0.0 772.0402840 .3000000000 0.0 0.0  &
```

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```
        0.0 25.00000000 25.00000000

STREAM FEED
    SUBSTREAM MIXED TEMP=298. PRES=0.9 MOLE-FLOW=100.
    MOLE-FRAC METHA-01 1.

BLOCK REAC-DIS RADFRAC
    PARAM NSTAGE=30 ALGORITHM=STANDARD MAXOL=25 DAMPING=NONE
    COL-CONFIG CONDENSER=TOTAL
    FEEDS FEED 2
    PRODUCTS DIST 1 L / BOTT 30 L
    P-SPEC 1 0.9
    COL-SPECS QN=1.5 <kW> MOLE-RR=4.
    REAC-STAGES 2 21 R-1
    HOLD-UP 2 21 MASS-LHLDP=140. <gm>

EO-CONV-OPTI

REPORT NOINSERT NOADA

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC

PROPERTY-REP PCES

REACTIONS R-1 REAC-DIST
    PARAM SUBROUTINE=USRKNT
    REAC-DATA 1 KINETIC
    STOIC 1 METHA-01 -2. / DIMET-01 1. / WATER 1.
;


  BLOCK:  REAC-DIS MODEL: RADFRAC
  -----------------------------
     INLETS   - FEED      STAGE   2
     OUTLETS  - DIST      STAGE   1
              BOTT      STAGE  30
    PROPERTY OPTION SET:   NRTL       RENON (NRTL) / IDEAL GAS

                    ***   MASS AND ENERGY BALANCE   ***
                        IN            OUT        GENERATION   RELATIVE
DIFF.
    TOTAL BALANCE
    MOLE(MOL/HR  )       100.000       100.000       0.00000
0.142109E-15
    MASS(KG/HR   )       3.20422       3.20422
0.277191E-15
    ENTHALPY(WATT    )   -6622.59      -6574.48                     -
0.726525E-02


                    ***  CO2 EQUIVALENT SUMMARY ***
     FEED STREAMS CO2E              0.00000     KG/HR
     PRODUCT STREAMS CO2E           2.20347     KG/HR
     NET STREAMS CO2E PRODUCTION    2.20347     KG/HR
```

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```
 UTILITIES CO2E PRODUCTION        0.00000      KG/HR
 TOTAL CO2E PRODUCTION            2.20347      KG/HR




                       *********************
                       ****  INPUT DATA  ****
                       *********************


   ****   INPUT PARAMETERS   ****

   NUMBER OF STAGES                                   30
   ALGORITHM OPTION                                   STANDARD
   INITIALIZATION OPTION                              STANDARD
   HYDRAULIC PARAMETER CALCULATIONS                   NO
   INSIDE LOOP CONVERGENCE METHOD                     NEWTON
   DESIGN SPECIFICATION METHOD                        NESTED
   MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS             25
   MAXIMUM NO. OF INSIDE LOOP ITERATIONS              10
   MAXIMUM NUMBER OF FLASH ITERATIONS                 30
   FLASH TOLERANCE                                    0.000100000
   OUTSIDE LOOP CONVERGENCE TOLERANCE                 0.000100000


   ****   COL-SPECS   ****

   MOLAR VAPOR DIST / TOTAL DIST                      0.0
   MOLAR REFLUX RATIO                                 4.00000
   REBOILER DUTY                  WATT                1,500.00

 **** REAC-STAGES SPECIFICATIONS ****

   STAGE  TO  STAGE              REACTIONS/CHEMISTRY ID
     2         21                      R-1

 **** HOLD-UP SPECIFICATIONS ****

   STAGE  TO  STAGE     LIQUID HOLDUP      VAPOR HOLDUP
     2         21         0.1400 KG          MISSING


      *****   REACTION PARAGRAPH R-1      *****



        ****   REACTION PARAMETERS   ****

   RXN NO. TYPE          PHASE      CONC.    TEMP APP TO EQUIL
 CONVERSION
                                    BASIS            K
     1    KINETIC       LIQUID      MOLAR

       ****   STOICHIOMETRIC COEFFICIENTS   ****

   RXN NO.    DIMET-01     METHA-01      WATER
     1        1.000       -2.000        1.000
```

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```
****     PROFILES    ****

 P-SPEC              STAGE   1  PRES, MPA                    0.90000

                        ******************
                        ****  RESULTS   ****
                        ******************


    ***    COMPONENT SPLIT FRACTIONS    ***

                            OUTLET STREAMS
                            --------------
                      DIST          BOTT
    COMPONENT:
    DIMET-01    1.0000        0.0000
    METHA-01    .99876        .12386E-02
    WATER       .83256E-04    .99992


    ***     SUMMARY OF KEY RESULTS     ***

     TOP STAGE TEMPERATURE          K                    316.258
     BOTTOM STAGE TEMPERATURE       K                    448.566
     TOP STAGE LIQUID FLOW          MOL/HR               208.676
     BOTTOM STAGE LIQUID FLOW       MOL/HR                47.8311
     TOP STAGE VAPOR FLOW           MOL/HR                 0.0
     BOILUP VAPOR FLOW              MOL/HR               147.657
     MOLAR REFLUX RATIO                                   4.00000
     MOLAR BOILUP RATIO                                   3.08705
     CONDENSER DUTY (W/O SUBCOOL)   WATT               -1,451.89
     REBOILER DUTY                  WATT                1,500.00

    ****    MAXIMUM FINAL RELATIVE ERRORS    ****

     DEW POINT                  0.45221E-05  STAGE=  3
     BUBBLE POINT               0.27025E-03  STAGE= 25
     COMPONENT MASS BALANCE     0.56913E-11  STAGE= 21 COMP=DIMET-01
     ENERGY BALANCE             0.43590E-04  STAGE= 26


    ****     PROFILES    ****

    **NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
              FROM THE STAGE INCLUDING ANY SIDE PRODUCT.


                                        ENTHALPY
STAGE TEMPERATURE   PRESSURE              J/KMOL              HEAT DUTY
      K             MPA           LIQUID        VAPOR          WATT

  1   316.26        0.90000     -0.20316E+09 -0.18306E+09  -1451.8855
  2   334.21        0.90000     -0.22236E+09 -0.18312E+09
  3   374.31        0.90000     -0.22894E+09 -0.18610E+09
```

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```
 29    448.41         0.90000        -0.27323E+09 -0.23648E+09
 30    448.57         0.90000        -0.27325E+09 -0.23666E+09   1500.0000
```

STAGE	FLOW RATE MOL/HR		FEED RATE MOL/HR			PRODUCT RATE MOL/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	260.8	0.000				52.1689	
2	263.8	260.8	100.0000				
3	248.5	216.0					
29	195.5	147.4					
30	47.83	147.7				47.8310	

```
     ****   MASS FLOW PROFILES   ****
```

STAGE	FLOW RATE KG/HR		FEED RATE KG/HR			PRODUCT RATE KG/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	11.71	0.000				2.3424	
2	9.623	11.71	3.2042				
3	8.050	8.762					
29	3.524	2.665					
30	0.8618	2.662				0.8617	

```
                      ****   MOLE-X-PROFILE    ****
```

STAGE	DIMET-01	METHA-01	WATER
1	0.91682	0.83100E-01	0.76331E-04
2	0.31807	0.67992	0.20009E-02
3	0.37029E-01	0.95086	0.12113E-01
29	0.23496E-14	0.66967E-03	0.99933
30	0.64258E-16	0.11240E-03	0.99989

```
                      ****   MOLE-Y-PROFILE    ****
```

STAGE	DIMET-01	METHA-01	WATER
1	0.99006	0.99366E-02	0.15009E-05
2	0.91682	0.83100E-01	0.76331E-04
3	0.60988	0.38772	0.23979E-02
29	0.11270E-12	0.50378E-02	0.99496
30	0.30899E-14	0.85018E-03	0.99915

```
                      ****   K-VALUES          ****
```

STAGE	DIMET-01	METHA-01	WATER
1	1.0799	0.11957	0.19664E-01
2	2.8820	0.12223	0.38149E-01
3	16.471	0.40776	0.19796
29	47.964	7.5228	0.99563
30	48.086	7.5640	0.99926

```
             ****    RATES OF GENERATION       ****
                       MOL/HR
```

STAGE	DIMET-01	METHA-01	WATER
1	0.000	0.000	0.000
2	0.1393E-01	-.2786E-01	0.1393E-01

```
     3    0.5844        -1.169         0.5844
    29    0.000          0.000          0.000
    30    0.000          0.000          0.000


                      ****   MASS-X-PROFILE      ****
   STAGE     DIMET-01       METHA-01      WATER
     1    0.94067       0.59301E-01    0.30626E-04
     2    0.40173       0.59728        0.98824E-03
     3    0.52665E-01   0.94060        0.67369E-02
    29    0.60053E-14   0.11905E-02    0.99881
    30    0.16431E-15   0.19990E-03    0.99980


                      ****   MASS-Y-PROFILE      ****
   STAGE     DIMET-01       METHA-01      WATER
     1    0.99307       0.69321E-02    0.58873E-06
     2    0.94067       0.59301E-01    0.30626E-04
     3    0.69266       0.30627        0.10650E-02
    29    0.28706E-12   0.89252E-02    0.99107
    30    0.78963E-14   0.15111E-02
0.99849
```

Appendix C: Fortran Kinetic Subroutine for Aspen Plus

```
C $Log: usrknt.f,v $
C Revision 1.3  1996/05/21  19:25:07  apbuild
C ANAVI 9.3 upgrade
C
C Revision 1.2  1996/04/26  19:15:09  apbuild
C Introduce 3phase modifications, Venkat
C
C ==========================cvs revision history=======================
C$ #3 BY: SIVA DATE: 15-NOV-1994 ADD DOCUMENTATION
C$ #2 BY: SIVA DATE: 21-JUL-1994 ADD X TO ARGUMENT LIST
C$ #1 BY: ANAVI DATE:  1-JUL-1994 NEW FOR USER MODELS
C
C     User Kinetics Subroutine for RADFRAC, BATCHFRAC, RATEFRAC
C     (REAC-DIST type Reactions)
C
      SUBROUTINE USRKNT (N,      NCOMP,  NR,     NRL,    NRV,
     2                   T,      TLIQ,   TVAP,   P,      PHFRAC,
     3                   F,      X,      Y,      IDX,    NBOPST,
     4                   KDIAG,  STOIC,  IHLBAS, HLDLIQ, TIMLIQ,
     5                   IHVBAS, HLDVAP, TIMVAP, NINT,   INT,
     6                   NREAL,  REAL,   RATES,  RATEL,  RATEV,
     7                   NINTB,  INTB,   NREALB, REALB,  NIWORK,
     8                   IWORK,  NWORK,  WORK)
C
C*********************************************************************
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C  OF THE ASPEN PLUS SUBSCRIPTION AGREEMENT.                          *
C*********************************************************************
C---------------------------------------------------------------------
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C         ASPEN TECHNOLOGY, INC.
C         CAMBRIDGE, MA
C---------------------------------------------------------------------
C
C    DESCRIPTION: TO CALCULATE REACTION RATES FOR KINETIC REACTIONS
C                 USING USER SUPPLIED SUBROUTINE
C
C     VARIABLES IN ARGUMENT LIST
C
C      VARIABLE  I/O  TYPE    DIMENSION    DESCRIPTION AND RANGE
C      N         I    I       -            STAGE NUMBER
C      NCOMP     I    I       -            NUMBER OF COMPONENTS
C      NR        I    I       -            TOTAL NUMBER OF KINETIC
C                                          REACTIONS
C      NRL       I    I       3            NUMBER OF LIQUID PHASE
C                                          KINETIC REACTIONS.
C                                          NRL(1): NUMBER OF
C                                                  OVERALL LIQUID
C                                                  REACTIONS.
C                                          NRL(2): NUMBER OF
C                                                  LIQUID1 REACTIONS.
C                                          NRL(3): NUMBER OF
C                                                  LIQUID2 REACTIONS.
C      NRV       I    I       -            NUMBER OF VAPOR PHASE
C                                          KINETIC REACTIONS
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C        T         I    R       -         STAGE TEMPERATURE (K)
C        TLIQ      I    R       -         LIQUID TEMPERATURE (K)
C                                         * USED ONLY BY RATEFRAC **
C        TVAP      I    R       -         VAPOR TEMPERATURE (K)
C                                         * USED ONLY BY RATEFRAC **
C        P         I    R       -         STAGE PRESSURE (N/SQ.M)
C        PHFRAC    I    R       3         PHASE FRACTION
C                                         PHFRAC(1): VAPOR FRACTION
C                                         PHFRAC(2): LIQUID1 FRACTIO
C                                         PHFRAC(3): LIQUID2 FRACTIO
C        F         I    R       -         TOTAL FLOW ON STAGE
C                                         (VAPOR+LIQUID) (KMOL/SEC)
C        X         I    R      NCOMP,3    LIQUID MOLE FRACTION
C        Y         I    R      NCOMP      VAPOR MOLE FRACTION
C        IDX       I    I      NCOMP      COMPONENT INDEX VECTOR
C        NBOPST    I    I       6         OPTION SET BEAD POINTER
C        KDIAG     I    I       -         LOCAL DIAGNOSTIC LEVEL
C        STOIC     I    R      NCOMP,NR   REACTION STOICHIOMETRY
C        IHLBAS    I    I       -         BASIS FOR LIQUID
C                                         HOLDUP SPECIFICATION
C                                         1:VOLUME,2:MASS,3:MOLE
C        HLDLIQ    I    R       -         LIQUID HOLDUP
C                                         IHLBAS    UNITS
C                                         1         CU.M.
C                                         2         KG
C                                         3         KMOL
C        TIMLIQ    I    R       -         LIQUID RESIDENCE TIME
C                                         (SEC)
C        IHVBAS    I    I       -         BASIS FOR VAPOR
C                                         HOLDUP SPECIFICATION
C                                         1:VOLUME,2:MASS,3:MOLE
C        HLDVAP    I    R       -         VAPOR HOLDUP
C                                         IHVBAS    UNITS
C                                         1         CU.M.
C                                         2         KG
C                                         3         KMOL
C        TIMVAP    I    R       -         VAPOR RESIDENCE TIME (SEC)
C        NINT      I    I       -         LENGTH OF INTEGER VECTOR
C        INT      I/O   I      NINT       INTEGER VECTOR
C        NREAL     I    I       -         LENGTH OF REAL VECTOR
C        REAL     I/O   R      NREAL      REAL VECTOR
C        RATES     O    R      NCOMP      COMPONENT REACTION RATES
C                                         (KMOL/SEC)
C        RATEL     O    R      NRLT       INDIVIDUAL REACTION RATES
C                                         IN THE LIQUID PHASE
C                                         (KMOL/SEC)
C                                         WHAT IS NRLT?
C                                         NRLT = NRL(1)+NRL(2)+NRL(3
C                                         NRLT IS NOT INCLUDED IN TH
C                                         ARGUMENT LIST.
C                                         * USED ONLY BY RATEFRAC *
C        RATEV     O    R      NRV        INDIVIDUAL REACTION RATES
C                                         IN THE VAPOR PHASE
C                                         (KMOL/SEC)
C                                         * USED ONLY BY RATEFRAC *
C        NINTB     I    I       -         LENGTH OF INTEGER VECTOR
C                                         (FROM UOS BLOCK)
C        INTB     I/O   I      NINTB      INTEGER VECTOR
C                                         (FROM UOS BLOCK)
C        NREALB    I    I       -         LENGTH OF REAL VECTOR
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C                                                    (FROM UOS BLOCK)
C        REALB    I/O   R          NREALB    REAL VECTOR
C                                                    (FROM UOS BLOCK)
C        NIWORK    I    I            -        LENGTH OF INTEGER WORK
C                                                    VECTOR
C        IWORK    I/O   I          NIWORK    INTEGER WORK VECTOR
C        NWORK     I    I            -        LENGTH OF REAL WORK VECTOR
C        WORK     I/O   R          NWORK     REAL WORK VECTOR
C
C***********************************************************************
C
      IMPLICIT NONE
C
C     DECLARE VARIABLES USED IN DIMENSIONING
C
      INTEGER NCOMP, NR,    NRV,   NINT,  NINTB,
     +        NREALB,NIWORK,NWORK
C
#include "ppexec_user.cmn"
      EQUIVALENCE (RMISS, USER_RUMISS)
      EQUIVALENCE (IMISS, USER_IUMISS)
C
C
C
C***********************************************************************
C
C
C
C
C     DECLARE ARGUMENTS
C
      INTEGER NRL(3),IDX(NCOMP),   NBOPST(6),
     +        INT(NINT),    INTB(NINTB),
     +        IWORK(NIWORK),N,      KDIAG, IHLBAS,
     +        IHVBAS,NREAL
      REAL*8 PHFRAC(3),     X(NCOMP,3),   Y(NCOMP),
     +       STOIC(NCOMP,NR),      RATES(NCOMP),
     +       RATEL(1),     RATEV(NRV),
     +       REALB(NREALB),WORK(NWORK),  T,     TLIQ,
     +       TVAP, P,     F,      HLDLIQ,TIMLIQ
      REAL*8 HLDVAP,TIMVAP
C
C     DECLARE LOCAL VARIABLES
C
      INTEGER IMISS
      REAL*8 REAL(NREAL),  RMISS
C
C     BEGIN EXECUTABLE CODE
C
      REAL*8 Cm, Cw, RATE, Kw, Ks
      Cm=13*X(2,3)
      Cw=13*X(3,3)
      Ks = 61200000*exp(-98000/(8.314*T))
      Kw = exp(-6.46+2964.0/T)
      RATE = HLDLIQ*Ks*Cm*Cm/((Kw*Cw+Cm)*(Kw*Cw+Cm))
      RATES(1) = RATE
      RATES(3) = RATE
      RATES(2) = -2*RATE

      RETURN
      END
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Product Data Sheet

AMBERLYST™ 35WET Polymeric Catalyst
Industrial-grade Strongly Acidic Catalyst

Description

AMBERLYST™ 35WET Polymeric Catalyst is a macroreticular, strongly acidic, cationic, polymeric catalyst. Its open continuous pore structure makes it an excellent heterogeneous catalyst for a wide variety of organic reactions. This catalyst possesses a novel acid functionality which gives it higher thermal stability than standard polymeric catalysts. Its polymeric structure is resistant to oxidants and breakdown caused by mechanical and osmotic shock.

AMBERLYST 35WET is a next-generation catalyst for the production of MTBE and TAME. It significantly outperforms conventional catalysts. AMBERLYST 35WET has increased activity which means throughput can be increased by 20 – 40% compared to AMBERLYST 15WET, while maintaining high olefin conversion. Selectivity to MTBE or TAME remains high.

Another important feature of AMBERLYST 35WET is that it increases the equilibrium constant of isobutylene and methanol to MTBE compared to conventional catalysts. This feature can lead to significant increases in MTBE productivity. Longer catalyst lifetimes may result from the increased concentration of acid sites and enhanced thermal stability.

Typical Physical and Chemical Properties[**]

Matrix	Styrene-divinylbenzene, macroporous
Type	Strong acid cation
Functional Group	Sulfonic acid
Physical Form	Black, spherical beads
Ionic Form as Shipped	H^+ Form
Concentration of Acid Sites [d]	≥ 5.40 eq/kg ≥ 2.1 eq/L
Water Retention Capacity	52 – 57%
Particle Size	
Particle Diameter [b]	700 – 850 µm
Uniformity Coefficient	≤ 1.5
< 425 µm	≤ 0.5%
> 1180 µm	≤ 2.0%
Nitrogen BET	
Surface Area	50 m^2/g
Pore Volume	0.35 cc/g
Pore Size, average	300 Å
Shrinkage	Water → Methanol : 4.5% Water → MTBE : 10.5% Water → Hexane : 21% Water → Dry : 40%
Bulk Density, as Shipped [c]	800 g/L

(left margin vertical text: For additional particle size information)

formation, please refer to the Particle Size Distribution Cross Reference Chart (Form No. 177-01775).

[c] As per the backwashed and settled density of the resin, determined by ASTM D-2187. [d]
Total Exchange Capacity (on a water-wet basis) ≥ 2.1 eq/L; Dry Weight Capacity ≥ 5.40 eq/kg.

Suggested Operating Conditions[**]

Maximum Operating Temperature	150°C (300°F)
Bed Depth, min.	100 cm (39 inches)
Operating Flowrate	1 – 5 BV*/h (LHSV)
Pressure Drop, max.	bar (15 psig) across the bed

* 1 BV (Bed Volume) = 1 m^3 solution per m^3 resin or 7.5 gal per ft^3 resin

Hydraulic Characteristics

Bed expansion of AMBERLYST™ 35WET Polymeric Catalyst as a function of backwash flowrate and water temperature is shown in Figure 1.

Pressure drop data for AMBERLYST 35WET as a function of service flowrate and water temperature is shown in Figure 2.

Figure 1: Backwash Expansion   **Figure 2: Pressure Drop**
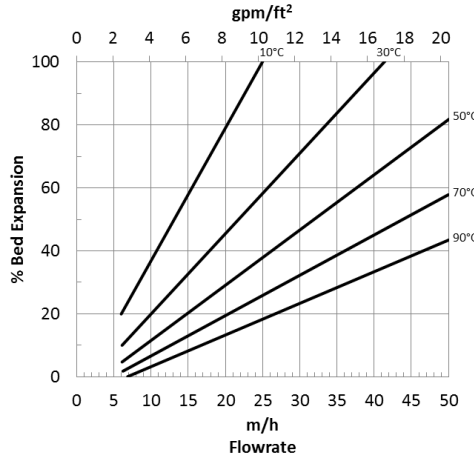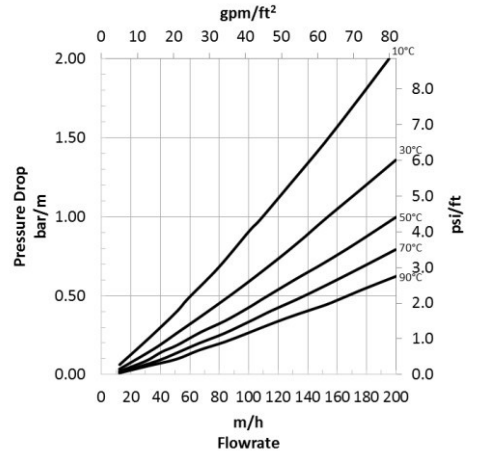
Product Stewardship

Dow has a fundamental concern for all who make, distribute, and use its products, and for the environment in which we live. This concern is the basis for our product stewardship philosophy by which we assess the safety, health, and environmental information on our products and then take appropriate steps to protect employee and public health and our environment. The success of our product stewardship program rests with each and every individual involved with Dow products—from the initial concept and research, to manufacture, use, sale, disposal, and recycle of each product.

Customer Notice

Dow strongly encourages its customers to review both their manufacturing processes and their applications of Dow products from the standpoint of human health and environmental quality to ensure that Dow products are not used in ways for which they are not intended or tested. Dow personnel are available to answer your questions and to provide reasonable technical support. Dow product literature, including safety data sheets, should be consulted prior to use of Dow products. Current safety data sheets are available from Dow.

WARNING: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.