Role of Liquid Saturation in Coke Yield from Model Vacuum Residue-Coke Agglomerates

by

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Abstract

The fluid coking process is an example of upgrading processes that use hot solids to heat and crack bitumen into more valuable products. When liquid is sprayed into a fluid bed of hot solids, the solids tend to agglomerate. The reactions in these agglomerates are subject to complex heating, reaction, and disintegration processes. The behaviour of bitumen derived feeds, and mixtures of these feeds with fluid coke particles, was investigated by heating them in Curie point reactors in an induction furnace up to 530 °C. Small scale reactors of different geometries were fabricated from Curie point alloy to test dependence of mixture behaviour on different parameters. The yield of coke was measured as a function of the ratio of liquid to solid, heating rate, thickness of mixtures and feed type in reactors with machined wells. Coke yield increased with the fraction of bitumen feed. Coke yields were insensitive to heating rates from 5 to 120 °C per second and mixture thicknesses, at a constant final temperature. Bubbling was observed as the ratio of feed in the mixture was raised above a certain threshold, depending on the kind of feed used. Bubbling was found to increase with greater heating rates, but it had little effect on ultimate coke yield. Putting bitumen feeds in a reactor with micro channels machined into it showed the high intensity of bubbling they underwent during cracking. A Curie point reactor was also used to test for the formation of skin on surface of mixtures. No evidence of skin formation was found in the subsequent experiments. The coke yield and bubbling trends observed with varying fluid coke ratios, different feeds, and with multiple heating rates, gives insights for improvement of reactor performance by designing better feed systems for the fluid cokers.

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A lot of hard work and effort goes into making milestones achievable and projects a success. Luckily, for my thesis, a significant amount of these efforts were put in by some wonderful people -- in a multitude of ways, and although some of them might not realize the lasting impact they have had on this project, I cannot emphasize enough how immensely valuable their contributions have been – to me as well as to this project.

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1. Introduction

1.1 Importance of Alberta Oil Sands

Exploration and production of oil from unconventional resources have received significant attention over recent years. Rise in demand with time and the depletion of production from conventional oil fields has ensured emphasis on exploration of new resources. The estimate for oil consumption for 2014 has been around 92.7 million barrels a day and the forecast for 2020 is approximately 99.1 million barrels a day (IEA, 2014). The requirement is expected to be close to 115 million barrels per day in 2040 (EIA, 2013). Canada has the third largest oil reserves which are only next to those of Venezuela and Saudi Arabia (Figure 1.1), and is well positioned to contribute to the oil supply (Alberta Govt., 2014). It has seen a significant growth in its oil and gas industry in recent years. The current reserves stand at 178 billion barrels (NEB, 2003) and 95% of these reserves are located in Alberta (EIA, 2007), mostly in the form of oil sands. The reserves are concentrated in 3 regions in northeast Alberta together covering an area of 140,200 square kilometres. Of these, about 4800 square kilometres are mineable out of which only 767 square kilometres have been utilized till now (Alberta Govt., 2012).

Improvement in technology has made extraction of bitumen and production of synthetic crude from these deposits economically feasible but not as attractive as the production from conventional oil resources like those in the Middle East. Hence, there has been a great deal of focus on making all the processes involved in the oil sands production chain more economical and environmentally friendly. These improvements have the potential of significantly and positively increasing Alberta's oil sands' impact on the Canadian economy.

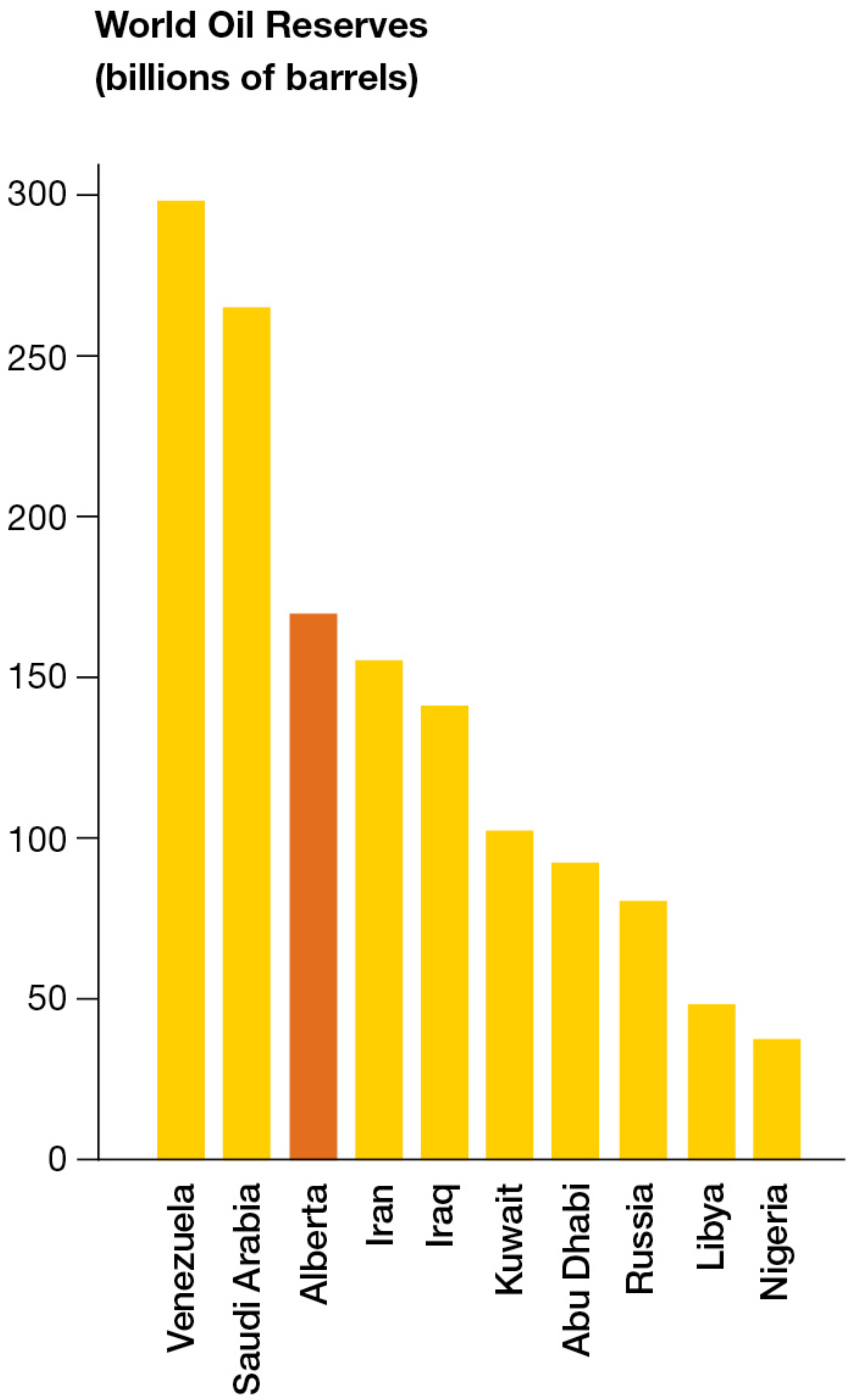

Figure 1.1 World Oil Reserves in 2014 *(Government of Alberta, 2014)*

1.2 Oil Sands versus Conventional Crude Oil

Oil sands are a mixture of sand, fine solids, clay and a heavy, viscous petroleum liquid (bitumen). Compared to conventional crude, which has an API of 32 (API is an inverse and expanded density scale used by the petroleum industry to fulfil the vital need of identifying small changes in densities (Equation 1.1)), bitumen is higher in specific gravity with an API of less than 10 (Table 1.1). Bitumen also has a significantly higher metal and sulphur content (Table 1.2) and a higher presence of non-distillable vacuum residue fraction. These factors reduce the market value of bitumen compared to conventional crude. Subsequently, bitumen is exposed to substantially more treatment before it is fit for consumption. The unique character of bitumen traces back to its origins. The original source rocks of oil sands are believed to be organic-rich shales in south-western Alberta. The organic matter in the shales over time give way to a material called kerogen (Gray, 2014). Cracking of kerogen leads to release of fragments which are the source of crude oil everywhere. In case of Alberta, oil from the shales in south-western Alberta flowed hundreds of kilometres to arrive at the present oil sands rich region in Northern Alberta during the Cretaceous period (Strauz et al., 2003; Adams et al., 2004; Gray, 2014).

Widespread bacterial action on the oil during its transportation process resulted in reduction of hydrogen content and increase in high molecular weight structures in the oil, which led to the formation of bitumen. Oil is subjected to this kind of biodegradation when it travels at depths of less than 600 metres and at temperatures below 80°C (Gray, 2014).

$$API = {}^{141.5}\!/_{specific\ gravity\ at\ 15.6\,℃} - 131.5 \qquad 1.1$$

Table 1.1 Comparison of API gravity, metal and sulphur composition between oils having different amounts of bacterial degradation *(Miller et al., 1987)*

Oil Type	**API Gravity**	**Vanadium (ppm)**	**Nickel (ppm)**	**Sulphur (wt. %)**
No Degradation	32	30.6	16.4	0.6
Moderate Biodegradation	12	224	75.1	1.6
Heavy Biodegradation (Bitumen)	4	137.5	68.5	1.5

Table 1.2 Properties of Athabasca Bitumen and Crude Oil *(Speight, 2007)*

Property	**Athabasca Bitumen**	**Crude Oil**
Specific Gravity	1.03	0.85-0.90
Viscosity (cp) 38°C (100°F) 100°C (212°F)	750,000 11,300	<200
Pour Point (°C)	10	-30
Elemental Analysis (wt. %)		
Carbon	83.0	86.0
Hydrogen	10.6	13.5
Nitrogen	0.5	0.2
Oxygen	0.9	<0.5
Sulphur	4.9	<2.0
Ash	0.8	0.0
Nickel (ppm)	250	<10.0
Vanadium (ppm)	100	<10.0
Fractional Composition (wt. %)		
Asphaltenes (pentane)	17.0	<10.0
Resins	34.0	<20.0
Aromatics	34.0	>30.0
Saturates	15.0	>30.0
Carbon Residue (wt. %) (Conradson Carbon Residue)	14.0	<10.0

1.3 Upgrading

Bitumen contains circa 50-60% by weight of vacuum residue (Gray, 2002). Vacuum residue cannot be distilled and needs to be converted into distillable fractions by chemical reaction. Upgrading is the process of conversion of bitumen into distillable fractions in order to produce synthetic crude oil before it is sent for refining. Conversion of bitumen to synthetic crude requires an increase in API from under 10 to 32. Reduction of the metals and sulphur content in the bitumen is also necessary. The series of upgrading operations required to accomplish these conversions fall into two distinct categories – primary and secondary upgrading. Primary upgrading is needed for removing the heavy fractions, metals and heteroatoms present in bitumen. Coking, hydroconversion, vacuum distillation, visbreaking, or a combination of these processes, are some of the ways to achieve this level of upgrading. Secondary upgrading might be required subsequently to produce synthetic crude oil, which involves removal of unwanted components like sulphur, nitrogen and oxygen. Common processes employed for secondary upgrading include hydrotreating, deep hydrogenation and catalytic hydrocracking. Hydrotreating, in contrast to hydroconversion, focuses on removal of specific heteroatoms, and not on cracking of feed. Consequently, the process is characterized by a temperature range well below the cracking temperatures ranges, i.e., temperatures less than 410°C, and usage of specific active metal supported catalysts.

Choice of the upgrading technologies for the industries depends on several factors. Bitumen is sometimes also sold without being exposed to any upgrading. This is usually done by adding a diluent to reduce its viscosity. Most of the bitumen from Canada is transported to United States making it an important stakeholder in the development of Alberta oil sands.

Recently, there have been concerns in the United States regarding the environmental impact of Canadian oil sands. One of the fears has been transportation of bitumen through pipelines. Americans are hesitant about having bitumen transported through their localities, viewing it as a toxic substance. The scenario makes upgrading in Canada even more vital as transportation of synthetic crude, being equivalent to conventional crude, has the possibility of being more receptive than transportation of bitumen. Some important factors on which upgrading processes are chosen are discussed below (Gray, 2014).

1. Capital cost – All oil sands projects require major investment costs and are only feasible when implemented at large scale. Reducing the number of steps involved in mining, extraction and upgrading operations can help in reduction of costs. For example, at Suncor and Syncrude, all the feed is forced through an upgrading process even though some of them do not require any cracking. Although modifications are now being made to route the distillable feeds to the vacuum distillation unit without passing them through the primary upgrader.
2. Bitumen and synthetic crude oil price differential – The price needed to upgrade bitumen into synthetic crude oil needs to be less than the price differential between selling bitumen and synthetic crude oil. A price differential of about $5 is required for the upgrading operations to be feasible. Present market conditions favour upgrading operations while opposite was the case in the early 1990s.
3. Coke production – Coke is a solid substance rich in carbon which forms as a by-product in some of the upgrading processes during cracking of bitumen. The coke tends to be higher in metal and sulphur content, and therefore utilizing coke in the most profitable way is a primary concern. Burning of coke for heat of combustion is

not always an option due to the environmental restrictions on the sulphur content. Syncrude and Suncor have the ability to store coke indefinitely because of their access to mines. However, companies like Husky, don't have this luxury and need to carefully monitor the quality of coke formed in the upgrading operations.

4. Production of high boiling residuum or pitch – Substances that have high boiling points form residues high in sulphur content after the upgrading operation. The residue formed from cracking operations has a lesser quality compared to original residue with a high softening temperature and lack of ductility. It becomes difficult for the residue to be sold for even asphalt applications. Presently, none of the products from the upgraders have an unconverted residue fraction in them.
5. Technology – Due to the scale of investments involved in the process, it is very important for the plant to operate as envisioned. Consequently, only technologies which have been tested multiple times and been successful are installed. New technologies have to succeed at demonstration scale before receiving the green signal.
6. Cost of hydrogen, natural gas and catalysts – The use of catalysts and hydrogen are essential to some upgrading operations. Hence, it is important to take into account the costs and the benefits associated with them. Since oil is traded on a volumetric basis, and hydrogen addition leads to volume expansion in product compared to the feed, employment of this kind of technology can be lucrative. However, on the other hand, the high costs of hydrogen utilized in the process also have to be taken into account.

Thermal cracking and coking of bitumen feeds find widespread usage in primary upgrading in North America. Delayed coking is used in Suncor while Syncrude employs fluid coking. The heavy reliance on coking technology for Canadian upgraders is due to its reliability and a relatively good grip on the ease of operation. The ability to handle different kinds of feeds including those having higher solid and water content and the lack of need of expensive catalysts make coking quite an attractive proposition for the oil sands industry. Delayed coking has lower setting up and operation costs which led Suncor to utilize this technology while better operating experience led Syncrude to adopt fluid coking (Gray, 2014; Syncrude Canada Ltd., 1998). Fluid coking, in contrast to delayed coking, makes use of a fluidized bed composed of hot coke particles with a higher temperature range of 500-550°C and a shorter residence time in the vapour phase for the cracked products. Hence, fluid coking generally tends to give a lower coke yield in its operation. However, better understanding of the mass and heat transfer interactions between liquid feed and the hot coke particles in the fluidized bed can led to improvement of the process to a more efficient one. This thesis focuses on understanding some of these interactions happening in the fluid coking process.

Table 1.3 Comparison of Primary Upgrading Processes *(Table from Gray, 2014)*

Technology	**Capital Cost**	**Operating Complexity**	**Operating Pressure**	**Operating Cost**	**Volume Yield on 525°C+**	**Units in Operation Worldwide**
Delayed Coking	Low	Medium	350 kPa	Low	80%	137
Visbreaking	Low	Low	350 kPa	Low	60%	186
Fluid Coking	Medium	Medium	350 kPa	Low	86%	8
Flexicoking	Medium	Medium	350 kPa	Low	85%	5
Canmet	High	High	14-21 Mpa	High	105%	Demo only
Veba	High	High	14-21 Mpa	High	105%	Demo only
LC- Fining and H-Oil	High	High	14-21 Mpa	Very High	100%	8

1.4 Influence of Production Processes on Upgrader Feeds

There are many processes which take place before the oil sands deposits find their way to an upgrader in the form of bitumen. Some of these have a significant influence on bitumen composition, which has the potential to affect reactor performance in an upgrader. In surface mining operations, widely used to take out oil sands ore from deposits, the bitumen is extracted by crushing the mined ore and mixing it with warm water. Subsequently, the mixture is passed through a conditioning pipeline to break lumps of oil sands releasing trapped bitumen in the process. The bitumen undergoes stages of gravity separation producing froth consisting of bitumen, water and fine clay particles.

The method adopted for separation of water and the clay particles from bitumen influences the composition of bitumen entering an upgrader. For example, in a naphtha based froth treatment, naphtha and bitumen are mixed in the ratio of 0.65-0.7 at about 75-80°C to reduce the viscosity of bitumen for separation of mineral solids and water from the bitumen (Gray, 2014). Centrifuges and inclined plate settlers are used to enable the separation of the constituents. The final product, i.e., bitumen in this process has a high water content of 3.5-5.5% and a fine solids content of 0.5-1.2%. The water in the bitumen is flashed off to give a product rich in fine solids and the salts that were present in the water. The feed is acceptable for upgrading plants downstream if the salts content is within a reasonable limit.

Paraffinic froth treatment, conversely, involves addition of paraffinic solvents like hexane to the froth. The solvent facilitates the precipitation of asphaltenes from the bitumen. About 7-9% of bitumen by weight precipitates and flocculates in the process and the flocculate then tends to absorb all the fine solids and water with it leaving bitumen behind, devoid of the aforementioned impurities. The bitumen resulting from the paraffinic froth treatment process has significantly lower water and fine solids content, and lesser metal content due to elimination of metal rich asphaltenes, in comparison to the naphtha process. However, the tailings in this case, consequently have a high mineral content and need to be processed before asphaltenes in the tailings can be used as marketable fuel.

The difference in water and fine solids content between the bitumen coming from the two froth separation processes is an important factor for determining the kind of upgrading operations needed for them, and the behaviour they would exhibit in such processes. For example, a high water and solids content in bitumen is handled better by thermal cracking processes compared to hyrdoconversion processes. The upgrading operations and their dependence on bitumen composition are discussed in detail in later chapters.

Steam assisted gravity drainage (SAGD), which consists of in situ production from oil sands deposits, has lower sand and clay composition in the bitumen that goes to the upgraders (Gray, 2014). The reason behind this lies in the geometry of the process. Oil is taken out from under the ground with the help of steam which is pumped into deposits to raise the temperature and reduce the viscosity of oil to allow it to flow. SAGD utilizes horizontal wells to inject steam into the deposits. The hot, less viscous oil is collected from another horizontal well located about 3-5 metres below the steam injection well which provides for a very gentle flow minimizing production of sand and clay (Gray, 2014). In situ upgrading of oil sands is a potential idea which proposes upgrading of bitumen directly in the oil sands formation. One of the successful pilot projects in this area has been carried out by Shell. Vertical heating wells are used to heat the formation at a range of 350-420°C which cracks oil in the formation into lighter products. The method has a lot of potential and can be environmentally friendly if the heating wells use nuclear energy as a heating source. The process also has the scope of significantly changing the quality of feed going into the upgraders. Xia and Greaves (2006) showed that in situ upgrading can increase the API of bitumen by an average of 8°, and also reduce the viscosity to less than 200 cp.

1.5 Objectives

Fluid coking is used on a large scale by Syncrude at its operations north of Fort McMurray, AB. As stated earlier, liquid feed is sprayed into a fluidized bed of hot coke particles, which provide the high-temperature conditions to convert the vacuum residue components and vaporize the lower boiling fractions of the feed (Dunlop et al., 1958). Reaction temperatures are in the range from 500-550°C (Gray, 2002). Liquid feed sprayed into a fluidized bed of particles can spread to give a thin film on the surface, or form bridges between particles and become trapped within agglomerates (Mohagheghi et al., 2014; Bruhns and Werther, 2005; Ariyapadi et al., 2003; Knapper et al., 2003). Ali et al. (2010) found that reaction of vacuum residue in model agglomerates of coke particles with 8-12.5 wt.% initial liquid content gave higher coke yield than in thin films of the same reactant. The difference was likely due to the retention of more cracked products in the liquid phase within solid-liquid agglomerates. Coke yield in the model agglomerates was insensitive to initial liquid concentration, which in this study was 20% to 30% of liquid saturation in a packed pellet of coke particles. Higher liquid saturations would be expected to give an even greater distance for the cracked products to diffuse to the free liquid surface, and possibly to drive bubbling due to saturation of the liquid phase with volatile components.

This thesis presents an experimental study into the relationship between liquid saturation of mixtures of coke particles with liquid bitumen feeds, and the final yield of coke at long reaction times. When liquid is sprayed into a fluidized bed, a wide range of local liquid saturations could occur, beyond the range examined by Ali et al. (2010). In this study we examined the range from 30% to 60% of the pore volume filled with liquid, and studied several bitumen-derived feeds at different heating rates. In each case, the reaction was allowed to proceed to completion and the ultimate coke yield was determined gravimetrically.

The study aims to validate the yield loss in products expected from agglomeration in reactors in Syncrude's fluid coking process.

1.6 Thesis Framework

The thesis is divided into 5 chapters. Background knowledge and literature review of upgrading processes and their bitumen chemistry is discussed in the next chapter, with focus on fluid coking. Experimental procedures, materials and techniques used are detailed in the third chapter. The fourth chapter comprises the results of the experiments and accompanying pertinent discussions. The thesis concludes with the fifth chapter which summarizes the findings of the research project, explores implications and suggests future work.

2. Literature Review

2.1 Upgrading Processes

The upgrading processes can be broadly classified into two distinct categories. The first set solely uses thermal energy for cracking of vacuum residues during upgrading while the second type makes use of heat and hydrogen in the presence of a catalyst to convert heavy fractions into lighter ones. Suncor uses delayed coking for its upgraders while Shell makes use of hydroconversion of vacuum residue in Canada. Syncrude has thermal based fluid cokers as well as a hydroconversion unit for upgrading bitumen feed. Both approaches have their share of advantages and disadvantages. The addition of hydrogen in hydroconversion results in a significant increase in volume yield of the product which makes the process profitable. However, hydrogen as a source is an expensive commodity and has the potential of negating the increase in value due to volume yield increase. Thermal cracking and coking processes, meanwhile, give lower volume yields but can handle feeds high in solid and water content. Expensive catalysts or expensive equipment needed for high pressure operations are also not required. Coking is the cheaper option but with low product yield while hydroconversion provides higher liquid yields but with higher associated expenses.

2.1.1 Thermal Cracking and Coking

Thermal cracking processes vary in severity based on the outcome desired. The process of visbreaking is mild and is used to reduce the viscosity of bitumen before it is sent for further upgrading. Coking processes are comparatively severe and disproportionate the feed into lighter ends, liquid products, and solid coke. The liquid products are processed further to obtain synthetic crude oil.

2.1.1.1 Visbreaking

Vacuum residue has a high viscosity at room temperature. It is attributed to the presence of entanglements between high molecular weight components in oil and formation of ordered chains in the liquid phase (Gray, 2014). The side chains present in asphaltenes and the bridging linkages can be removed by 5-10% conversion of vacuum residue to the lighter naptha fraction. The conversion is accomplished by visbreaking, which achieves a substantial decrease in viscosity of bitumen. Temperatures range from 475-500°C in the reactor but the residence time is short ranging from 1-3 minutes. Pressure ranges from 0.7 MPa to 5 MPa. A lower pressure results in reduction of residence time in the liquid phase.

The milder conditions employed result in a fivefold decrease in the viscosity of oil. Shorter residence times prevent coking and polymerization reactions. Hence, the conversion of bitumen to distillates is not significant. However, it is difficult to prevent coking completely inside the reactor tubes and decoking is required every 3-6 months. Additives can be added to suppress coke formation (Allan et al., 1983). The product from visbreaking operations is unstable in nature and has the tendency to precipitate asphaltenes (Wiehe, 2008). The product also has affinity towards polymerization reactions upon storage leading to formation of tars and gums. Consequently, the product may have a higher viscosity than intended (Henderson and Weber, 1965). Addition of diluent can lead to further decrease in viscosity in such cases (Rhoe and de Blignieres, 1979).

2.1.1.2 Delayed Coking

Coking is widely employed for primary upgrading of heavy oils and bitumen as it is a very good mineral solids and metals rejection process. These substances are absorbed from the feed by coke making the distillates almost free of them. An important point to note is that coke is also rich in carbon content although it does not result in any reduction in percentage carbon content of liquid distillates in comparison to the incoming feed. The extra carbon content in coke is compensated by the low percentage of carbon and high percentage of hydrogen in the gas products. Delayed coking is popular especially when there is demand for the coke produced. Industries involved in graphitic carbon manufacture are good markets for the delayed coke.

The feed is kept in the liquid phase for long amounts of time in coke drums to allow thermal cracking to take place. Feed disproportionates into gas, liquid product and coke in a semi batch process (Figure 2.1) where the feed is preheated in a heater to about 500°C after being passed through a fractionator. It is then sent to a coker drum. There are at least two coker drums present in a delayed coking operation. As the reaction proceeds, the inline drum gets filled by coke while the other drum(s) is decoked and prepared for taking in feed. It takes about 48 hours for the drum to be filled up by coke. The lighter ends are sent to the fractionator again to be quenched by colder feed. Large cokers are required in Alberta for coking of bitumen feeds. Suncor employs 8 coke drums, each of which is 26 feet in diameter and operated in a 14 hours cycle (Gray, 2014).

Despite the requirement to have large cokers, the size of the drum cannot be increased indefinitely, because of the underlying thermal stresses developed due to

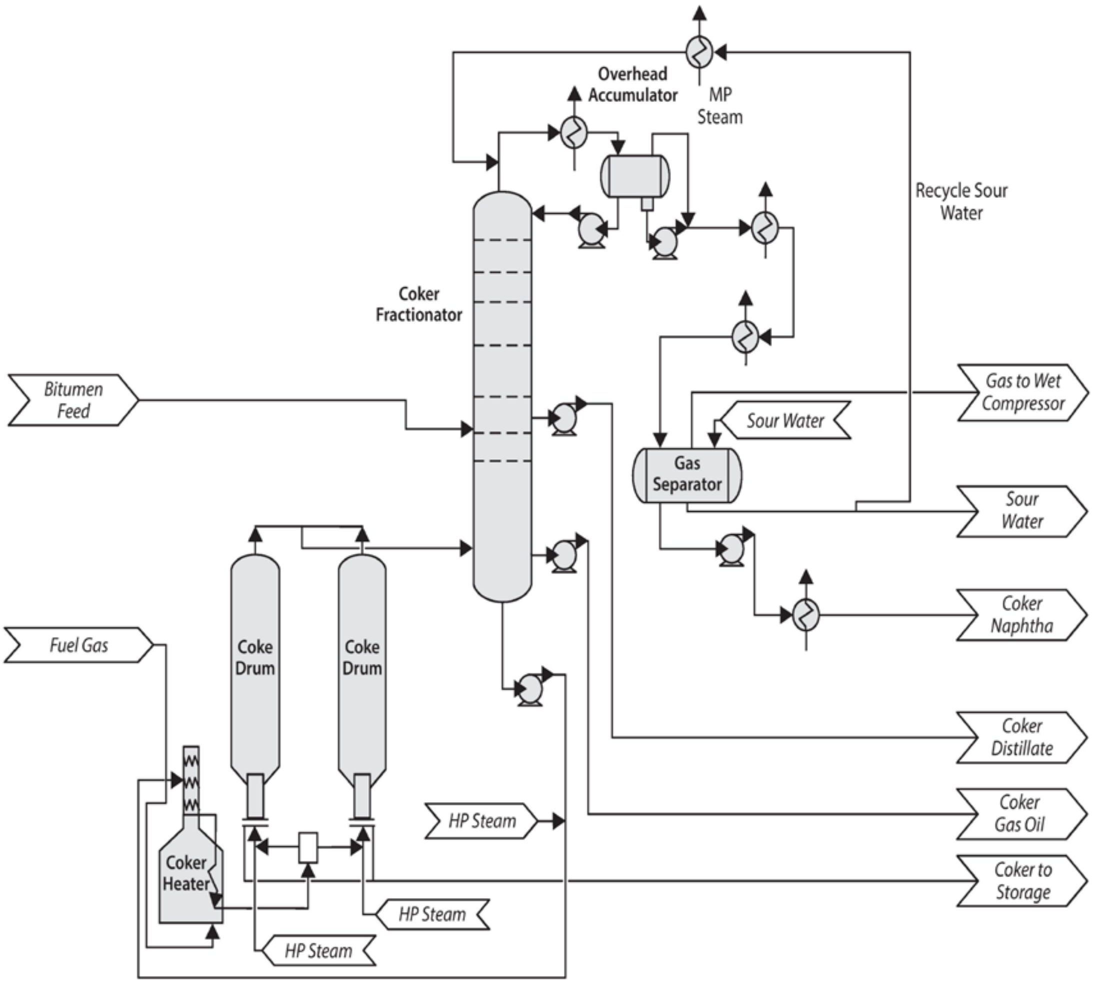

Figure 2.1 Schematic of Delayed Coking *(Upgrading Oil Sands Bitumen and Heavy Oil by Murray R. Gray. Copyright 2014, University of Alberta Press. Reproduced with permission of University of Alberta Press)*

constant cycles of heating and cooling a drum has to experience during coking and decoking.

Apart from the limitation in mechanical design for increase in size, a foam layer is formed in a delayed coker on top of the liquid layer during the coking cycle which reduces its capacity to process feed. Addition of silicone oil helps suppress foam formation but the effectiveness is significantly reduced due to its rapid decomposition under such conditions. Another problem requiring attention during the process is that of coking of tubes of the coke heater. Heated feed is required to be transferred to the drum quickly failing which the high temperatures allow coking to take place during transportation. Consequently, the tubes of the coke heater accumulate coke over time and have to be decoked to ensure smooth operation. Combustion of the deposits is an effective method used to clean the tube. Injection of steam to flush out the deposits into the coke drum is an alternative. Pigging, in which water is used to push the pigs through the tubes, produces the cleanest tubes but it is also one of the most time consuming processes.

2.1.1.3 Fluid Coking

Fluid coking utilizes a fluidized bed for thermal cracking of bitumen feeds. It is a continuous operation (Figure 2.2) unlike to delayed coking which is a semi batch process. Ease of operation is more in the fluid coking process since handling of large amount of feeds is easier in a continuous process. The process was developed by Exxon Mobil in the mid-1950s (Voorhies and Martin, 1953). Feed is sprayed into the fluidized bed consisting of hot coke particles with the help of steam assisted nozzles. The coke particles have a bulk density of 750-880 kg/m^3, and a particle density of 1440 kg/m^3.

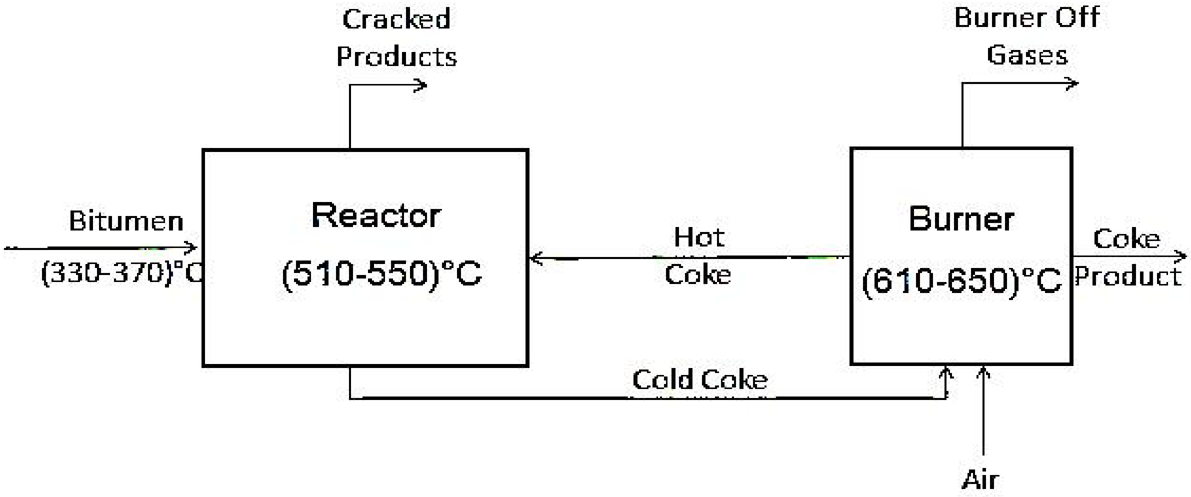

Figure 2.2 Schematic of Fluid Coking Process Cycle

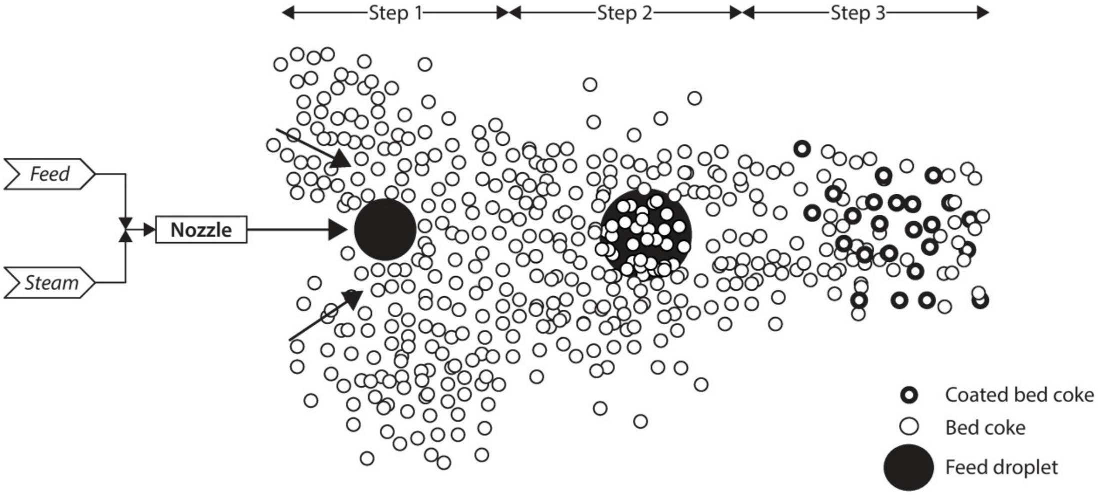

Figure 2.3 Spraying of feed in the fluidized bed full of coke *particles* *((Upgrading Oil Sands Bitumen and Heavy Oil by Murray R. Gray. Copyright 2014, University of Alberta Press. Reproduced with permission of University of Alberta Press)*

The diameter of particles range from 100-600 μm. Coking of the liquid feed takes place on the surface of these particles (Figure 2.3). The temperature of the coker is higher than that of delayed coker and varies in the range of 500-550°C. Spraying of feed onto the coke particles ensures enhanced surface area of contact for heat transfer. Heating is fast and product vapors tend to have shorter residence times. These conditions lead to higher product yields in this case relative to those from delayed coking.

Coke is sent back to the burner where it undergoes partial combustion at about 630°C, in limited air supply, giving a rich stream of carbon monoxide and hydrogen gas. Remaining coke particles get heated and are sent back into the fluidized reactor to maintain its temperatures. Circulation rate of coke is very high compared to the feed that goes in and the new coke deposited on the coke particles is about 2.8% by weight of the total coke that goes per pass through the reactor (Gray, 2014). The cracked products rise to the top of the reactor where they are passed through cyclones to remove the entrained coke particles (Figure 2.4). The next stage is the scrubber section where the vapors are quenched by relatively cooler fresh feed or condensed liquid.

A major limitation in the process is the sulphur dioxide released during the partial combustion of coke in the burner. The level of sulphur emissions initially produced by Syncrude’s cokers is no longer legally acceptable because of environmental concern. Therefore, flue gas desulphurization or gasification has to be used to reduce sulphur emissions. The latest unit of Syncrude uses ammonia for desulphurization to produce ammonium sulphate. Deposition of coke on the inner walls of the reactors is also a challenging problem. The coke deposits can get as thick as a metre and have to be periodically removed every 2-3 years. Fouling is a major concern for the industry as it can significantly affect the performance of the reactor. Feed distribution inside the reactor and agglomerate formation can greatly impact the rate of fouling. Its mechanism and subsequent possible methods to reduce it are discussed in detail in Section 2.4 and Section 5.2.

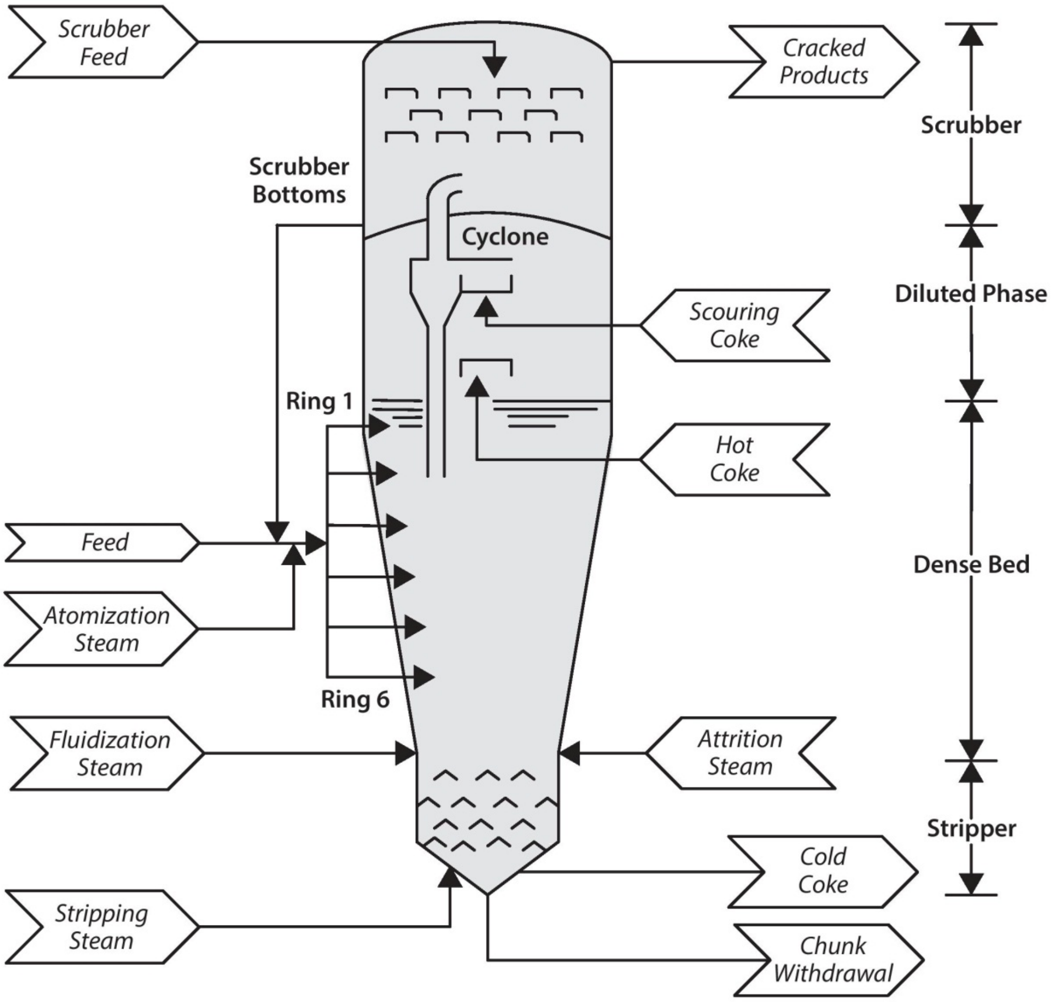

Figure 2.4 Schematic of Fluid Coker *(Upgrading Oil Sands Bitumen and Heavy Oil by Murray R. Gray. Copyright 2014, University of Alberta Press. Reproduced with permission of University of Alberta Press)*

The use of a fluidized bed of heated coke particles to crack bitumen feeds has many salient benefits. Due to the increased surface area of contact between the feed and the coke particles, there is excellent transfer of heat ensuring rapid heating of the feed. Residence time of the cracked products is also reduced in the vapor phase which prevents further cracking of products to the less valuable lighter ends. However, the process has scope for improvements, and there are coking processes under development, testing or early stages of implementation which are based on the same fundamental principles fluid coking is based on, albeit with certain variations. These technologies have been discussed in the succeeding sections to provide an insight into the possible future of the fluid coking process.

2.1.1.4 Flexi Coking

Flexi Coking is a process, invented by Exxon Mobil, and very similar to fluid coking, except for the presence of a coke gasifier to convert the coke into CO, CO_2 and H_2. Limited amount of air is supplied to the gasifier to maintain temperatures of 830-1000°C. These conditions create a reducing environment converting sulphur into hydrogen sulphide. Product yields are the same as that in fluid coking because the reactor, which is the same as in fluid coking, is unaffected by the gasifier. Emission of sulphur dioxide is mitigated in the process but installing a gasifier can be expensive. In addition, coke remaining post gasification, although less, will still be higher in sulphur content than that of the feed making the process even less attractive, especially for Alberta where the price of natural gas is very low.

2.1.1.5 Lurgi-Ruhrgas Process

Performance of a coking process can be improved by reducing the residence time of product vapors in the reactor. The longer the cracked products stay in the reactor, the greater will be their tendency to crack to give the less valuable lighter ends making it important to reduce the residence time of vapors in the reactor. LR process attempted to accomplish it by having a mechanical stirrer mixing the hot solid particles, acting as heat carriers, and feeds together (Wiehe, 2008). The process is good for feeds having high solids content or poor flow properties. The limitation, however, is in the size of the reactors that can be constructed and operated in this process due to the presence of mechanical mixers.

Usage of LR process has also been considered for conversion of asphaltene and residue fractions of bitumen (Weiss et al., 1998). It uses hot circulating coke for cracking of bitumen feeds. LR-Mixer reactor has two screws for doing the mixing. The screws clean each other as well as the interior of the reactor. Partial flash vaporization of feedstock takes place followed by coking of asphaltenes and residue to give additional oil, gas and coke (Pagel, 2000). Pilot plants of the LR process exist in the research facilities of Exxon Mobil but the first commercial attempt to use this technology, at Esso Ingolstadt refinery in Germany, failed due to the intensity of fouling occurring (Ali, 2010).

2.1.1.6 ART Process

ART is also an upgrading process developed to reduce residence time of feed in the reactor. The process is similar to fluid catalytic cracking, except that it uses hot inert solid particles instead of catalysts. The particles quickly heat up the feedstock. The resulting cracked products and coke formed is separated. The products get quenched while the coke deposit on the heat carriers is burnt off in a combustion vessel. The metal deposits on the inert particles from the feedstock make them gradually inefficient and hence, carrier is replaced in parts periodically. The process was developed by Engelhart (Dennis, 1988; Bartholic, 1981). In terms of commercialization, operations at an Ashland Petroleum Refinery using a revamped FCC unit, was shut down due to fouling problems (Wiehe, 2008).

2.1.1.7 Ivanhoe Heavy to Light Process

Ivanhoe HTL is a process similar to fluid coking developed by Ivanhoe Energy's sister company Ensyn Group Inc. Since their merger in 2005, Ivanhoe Energy is in control of the intellectual property of this process with regards to upgrading of heavy oils. The process uses silica particles as heat carriers instead of coke or other inert particles. It also simultaneously burns the coke formed in the cracking reactions to produce on-site energy and hence, is a good candidate for integration of upgrading processes with upstream operations. The first successful demonstration of the capability of this process to upgrade heavy oil was carried out by Ensyn in the late 1980s (Ivanhoe Energy, 2014). A 1,000-barrel-per-day Commercial Demonstration Facility (CDF) was commissioned in Belridge heavy oil field in Southern California in 2004 with good results. And subsequent testing was done with upgrading of Athabasca bitumen. In terms of commercialization, in 2012, Ivanhoe Energy started a project in Republic of Guatemala to implement HTL technology to upgrade heavy oil.

2.1.1.8 I^{y}Q Upgrading by ETX Systems

I^{Y}Q Upgrading formerly known as ETX Upgrading is an improvement on the fluid coking process, developed by ETX Systems, Calgary. In the process, there is a cross flow movement of heated solid particles across the reactor while feed is sprayed from the top of the reactor. Fluidization gas is introduced from the bottom of the reactor. The arrangement allows sufficient time for liquid feed to completely crack on the surface of the hot particles, which may either be sand or coke. The fluidization gas ensures quick removal of the product vapors from the reactor to prevent over cracking. It ensures a higher quality as well as higher yield of liquid products compared to other coking processes. The process has been tested on 1 barrel/day scale and is now moving into field pilot project with a capacity of 1000 barrels/day in Alberta with a design basis memorandum completed in 2012 (ETX Systems, 2014).

These technologies show that a lot of research is going on into the development of new cracking processes based on the concept of fluidized bed providing heat transfer as in fluid coking. However, the attempts have not been very successful yet although some carry promise. The scale of investments needed for setting up a plant operating on a new technology compared to well proven and tested processes such as delayed and fluid coking also acts as a deterrent in evolution of new technologies compared to the cheaper incremental modifications done to existing processes.

2.1.2 Hydrogen Addition Processes

Hydrogen addition to bitumen feeds in presence of catalysts is also an important route for upgrading of these feeds. Depending on the operating conditions employed in the upgrading process, different purposes can be served through the process of hydrogen addition.

2.1.2.1 Hydroconversion

Hydroconversion is a primary upgrading process which involves simultaneous thermal cracking of bitumen feeds and hydrogenation of aromatics. Removal of sulphur and nitrogen also take place to an extent. Temperature ranges are typically above 410°C. The catalysts assist the hydrogenation taking place in the reactor. However, they do not provide much help in cracking reactions since cracking catalysts are poisoned by the nitrogen present in the feed. Significant suppression of coke formation takes place during the process due to presence of hydrogen, higher pressures in the range of 10-20 MPa (Panariti et al., 2000), and addition of molybdenum with hydrogen (Kriz and Ternan, 1992). Addition of catalysts in the reactor may be on fixed bed or a catalytic ebullated bed. A fixed bed is not recommended for Alberta bitumen because of its high mineral solids content which has the potential of clogging the spaces between catalyst pellets, which may lead to rapid shutdown due to the huge pressure drop created. Hence, catalyst is always in a fluidized state in plants processing bitumen feeds. Two variations of the ebullated bed design are used in the industry currently, i.e., H-Oil and LC-Fining, with the differences being in equipment design. The cracking reactions in the hydroconversion process result in production of lighter ends like methane, ethane and propane. These gases contaminate the hydrogen recycle stream and therefore, pressure swing adsorption is used to purify the recycle stream. Additionally, make up hydrogen is added to it to maintain the partial pressure of hydrogen in the reactor. Hydroconversion processes always give a product yield of more than 100% on a volumetric basis which translates into more profit margins for industries. However, the gains made are compensated by the expensive hydrogen that needs to be used in the process.

2.1.2.2 Hydrotreating

Hydrotreating is a secondary upgrading process which accepts feed from primary upgrading processes. It is used for removal of sulphur and nitrogen from distillate feeds and hydrogenation of olefins and aromatics. Since there are no cracking reactions needed, the conditions are milder with a temperature range below 410°C, and a higher partial pressure of hydrogen. These conditions accompanied by a significantly cleaner feed provide for longer catalyst life times.

2.2 Chemistry of Bitumen Upgrading

The upgrading processes discussed in the previous sections were based on two approaches. They worked either on the principle of thermal cracking or hydrogenation of feed in the presence of catalysts. Consequently, the chemistry of bitumen upgrading is divided into these two categories. In case of thermal cracking, the C-C bonds are broken without the help of any catalysts, and significant rates of such reactions occur only above 420°C due to the high strength of these bonds as shown in Table 2.1. Hence, reaction temperatures are above 420°C for cracking reactions to take place. The reactions proceed via free radical mechanism. Hydrocarbons in the liquid and vapor phase undergo bond dissociation to form highly reactive radical intermediates. The reaction is quite unfavourable and the radicals formed are short lived and in low concentrations. Nevertheless, it is sufficient to initiate a chain reaction converting a large percentage of the feed to lighter fractions.

Table 2.1 Bond Dissociation Energies *(Benson, 1976)*

Chemical Bond	Energy (kcal/mol)	Energy (kJ/mol)
C-C (aliphatic)	85	355.6
C-H (n-alkanes)	98	410.3
C-H (aromatic)	110.5	462.3
C-S	77	322.2
C-N (amine)	84	351.5
C-O (methoxy)	82	343.1

The free radical mechanism via which these reactions take place is shown below (Gray, 2014):

Stage 1 – Initiation

$$A \overset{k_1}{\rightarrow} 2R\cdot$$

Stage 2 – Propagation

Hydrogen Abstraction $R\cdot + A \overset{k_2}{\rightarrow} RH + A\cdot$

β-Scission $A\cdot \overset{k_3}{\rightarrow} R\cdot + B$

Stage 3 – Termination

Possibility 1 $R\cdot + R\cdot \overset{k_4}{\rightarrow} Products$

Possibility 2 $R\cdot + A\cdot \overset{k_5}{\rightarrow} Products$

Possibility 3 $A\cdot + A\cdot \overset{k_6}{\rightarrow} Products$

In the above reaction mechanism, A represents the initial alkane. A· is the corresponding radical formed. R· is the lower alkyl radical formed while RH is the corresponding alkane. B represents the olefins formed in the reaction. Ease of thermal cracking of molecules depends on the strength of the bonds being broken which can be gauged from the bond dissociation energies shown in Table 2.1. In the reaction mechanism, the initiation step, i.e., the formation of radicals is an energy unfavourable state and the radicals exist only in low concentrations for very short durations. But they are important nevertheless because of their tendency to undergo chain reactions. Despite the difficulty in initiation, there may be multiple propagation steps for each bond broken and it is also more kinetically favourable.

As shown in the β- Scission step, the bond breakage on the parent radical takes place at a β position from the radical centre giving rise to an olefin and a smaller alkyl radical. An important behaviour of the free radical mechanism is that they tend to have simple kinetic expressions for even complex pathways. The apparent reaction order is usually first order for the cracking reactions.

Aromatic hydrocarbons react in a similar way to aliphatic hydrocarbons in cracking reactions. The side chains crack to give lower alkyl aromatics and olefins, and the aromatic groups do not crack under normal cracking conditions. Thiophenic sulphur is similar and resistant to cracking under the normal conditions. However, thiols, sulphides and disulphides are quite reactive under these conditions due to the relatively weaker C-S bond (Table 2.1).The condition has very important implications in the thermal cracking of bitumen as thiols, sulphides and disulphides can be as high as 50% of the total sulphur content in bitumen feeds.

An important aspect of thermal cracking is the phase of the reactions taking place. Liquid phase cracking has a relatively higher density of hydrocarbons which increases the hydrogen abstraction reactions compared to β-Scission (Ford, 1986; Fabuss et al., 1964; Kissin, 1987). It results in a greater yield of liquid products. Vapor phase cracking experiences the opposite conditions in terms of hydrocarbon density and the type of reactions taking place. β-Scission is more prevalent leading to more of lighter ends in the cracked products. Due to such conditions, liquid phase cracking is always desired since the goal is to improve the yield of the valuable liquid product in the process. Low pressure, high temperatures conditions favor rapid vaporization of feed and cracking in the vapor phase. Consequently, yield of lighter ends are highest in low pressure coking processes. Also, the yield of gas oil in coking tends to be lower than those in hydroconversion processes.

2.3 Coke Formation

Toluene insoluble carbonaceous solids are referred to as coke but in the context of oil sands upgrading operations, the term is ascribed to the carbon rich solids which are formed on cracking of bitumen feeds. Coking removes mineral solids, metals and the heavy fractions in the feed which get deposited in the form of coke. Coke formation is an integral part of thermal cracking processes since it reduces the amount of undesired components of feed from getting into the liquid products. However, it is not desired in hydroconversion processes which focus on hydrogenation of as much fraction of the feed as possible. Coke formation in bitumen and vacuum residues take place in the liquid phase during cracking. There are two pathways to coke formation. The first is through polymerization reactions taking place in the lighter products formed and the second path is through reactions involving removal of side chains in the larger aromatic molecules in the feed, dehydrogenation of naphthenes, condensation of aliphatic structures, and condensation of aromatics – all of which lead to formation of aromatics. Coke formed through polymerization is called extrinsic coke while the coke formed from large aromatic molecules, usually having more than 5 rings, is termed intrinsic coke. While the coke formed from aromatic molecules is required in a thermal cracking process to separate the heavy fractions from the product yields in order to increase their hydrogen to carbon ratio, extrinsic coke is not desired since it is a recombination of lighter ends which diminish product yields. As mentioned earlier, polymerization reactions are preferred over β-Scission reactions in liquid phase cracking leading to a greater tendency of formation of extrinsic coke. Polymerization reactions affect the molecular weight of the molecules while condensation reactions have an effect on the hydrogen to carbon ratio of molecules.

As the reactions proceed, a phase separation occurs with the creation of aromatic rich liquid phase. Wiehe, 1993 mentions the importance of aromaticity in the phase separation process. Gray et al., 2002, on investigation however, discovered that poly-nuclear aromatic compounds were absent in the toluene insoluble phase. The finding suggests that molecular weight of the compounds, affected primarily by polymerization reactions, plays a vital role in coke formation. Addition of solvents also affects phase separation. Aromatic solvents tend to suppress phase separation while paraffinic solvents enhance it (Gray, 2014).

The reactions taking place in the toluene insoluble phase lead to formation of an additional phase known as the mesophase, which is distinct from the toluene insoluble material. The mesophase is in liquid-crystalline state and has been observed comprehensively in situ (Rahimi et al., 1998). Mesophase is absent in the early stages of formation of coke but gets important as the reaction proceeds (Liu, 2002). As the compatibility of the liquid phase increases with the aromatic molecules, mesophase character of coke eventually decreases (Lott and Cyr, 1992).

Presence of solids has a significant effect on coke formation. Hence, it is necessary to consider the nature of pre-upgrading processes (discussed in Section 1.4), involved in the production of bitumen, in upgrader design and operation. Previous studies have shown that solids tend to reduce the intensity of coke formation (Tanabe and Gray, 1997). Presence of solids has allowed higher severity operations in the process of visbreaking without deposition of coke on reactor surfaces (Sankey and Wu, 1989). Prevention of deposition of coke is due to the presence of solids in the bitumen feeds. The solids have a coating of organic material (Chung et al., 1998), which has a high affinity for coke. Consequently, this leads to entrapment of solid particles in the coke formed (Wang et al., 1998). As the solids get dispersed in the reactor, coke, in turn, gets dispersed significantly increasing its exposure to the hydrogen-transfer reactions from the liquid phase (Bi et al., 2007).

Coke formation varies with the kind of feed being introduced into the reactor. Methods have been devised to measure the coke forming tendency of a given feed. Feed is pyrolyzed under a specific set of conditions and the amount of solid residue left after reaction is measured as a fraction of the initial weight of the feed sample. Three popular methods are used to measure the coke forming tendency – Micro carbon residue (MCR), Conradson carbon residue (CCR), and Ramsbottom carbon residue (RCR). The difference among them lies in the apparatus and the heating rates used. MCR is the most common among them although the numerical values in the end are the same as that of CCR. In the determination of MCR, 150 mg of oil sample is placed in a glass tube and then weighed. The next stage comprises keeping the tube in an oven and heating it at a rate of 10-15°C/min in an atmosphere of nitrogen. Temperature is raised until the tube temperature reaches 500°C after which the temperature is maintained for 15 minutes. The system is then cooled and the tube with the remaining solid residue is weighed again. The fraction of solid residue to the initial weight of the sample is calculated which gives the MCR content of the particular feed.

2.4 Mass Transfer in Liquid Coke Mixtures in Fluid Coking

Revisiting the process of fluid coking, the mass transfer that takes place in the reactor during the interaction between the hot coke particles and the bitumen feeds plays a vital role in determining the nature and the yield of cracked products, the resulting coke, and the fouling taking place in the reactor. Coke particles which are 100-600 μm in diameter form an effective mode of heat transfer for thermal cracking of liquid feeds (Figure 2.6). They are able to provide a large surface area of contact for heat transfer to the feed. Feed is sprayed into the fluidized bed of hot coke particles with the droplet size ranging from 300-3000 μm depending on nozzle design (Tollefson et al., 1997). It is followed by conversion of vacuum residue components and vaporization of the lower boiling fractions (Dunlop et al., 1958). The liquid spreads among the hot particles in the reactor; the hot particles constitute the reaction surface, coated with thin films of reacting vacuum residue (Gray, 2002). The thickness of the liquid film formed on the surfaces is an important parameter in the mass transfer taking place with the liquid phase. Cracked products diffuse through thin films of feed, and when the films become too thick for molecular diffusion to release the

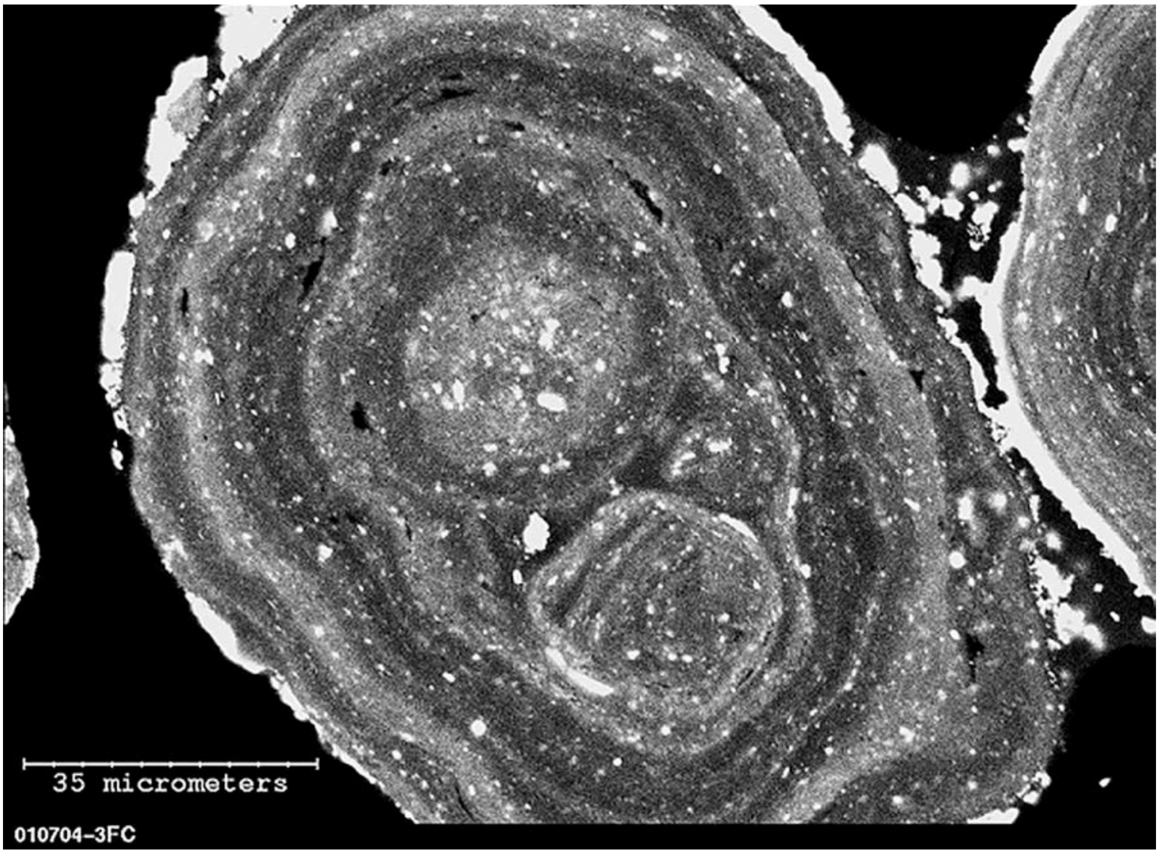

Figure 2.5 SEM of a cross section of a fluid coke particle showing granulation and deposition of coke layers *(Upgrading Oil Sands Bitumen and Heavy Oil by Murray R. Gray. Copyright 2014, University of Alberta Press. Reproduced with permission of University of Alberta Press)*

products, vapor bubbles nucleate and reaction-driven boiling occurs (Gray et al., 2001). The less efficient the transport of cracked products out of the reacting liquid is, the higher is the fraction of cracked products trapped by recombination reactions, which leads to higher coke yields. Gray et al. (2001) showed that there was a steady increase in coke yield with increase in film thickness from 20 μm to 80 μm when films of vacuum residue were coated on the interior of a stainless steel tube and rapidly heated to 530°C. Dutta et al. (2001) used isotopic tracers to confirm that more potentially valuable vapor products were trapped in the coke with the increase in feed film thickness from 15 μm to 150 μm. Radmanesh et al. (2008) demonstrated that these trends were consistent with recombination of cracked products as they diffused through the reacting liquid film, giving higher coke yields.

Within a fluidized bed reactor, liquid distribution is more complex than in a simple film geometry. Liquid feed sprayed into a fluidized bed of particles can spread to give a thin film on the surface, or form bridges between particles and become trapped within agglomerates (Mohagheghi et al., 2014; Bruhns and Werther, 2005; Ariyapadi et al., 2003; Knapper et al., 2003). On examination of cross section of coke particles, a uniform deposition of coke layers were found across all particles along with signs of agglomeration (Figure 2.5) (Gray, 2002). Thickness of coke layers were in the range of 2 to 10 μm. Gray (2002) calculated that an oil to coke ratio of about 0.1 kg/kg, and a uniform coating of Athabasca bitumen (density of 1016 kg/m^3) on coke particles having a diameter of 150 μm and a density of 1500 kg/m^3 would give an average film thickness of 4 μm. Post cracking reactions, the surviving coke layer would be around 0.4 μm thick. Ratio of film thickness to the final coke layer thickness would vary, and depend on the MCR content of the feed.

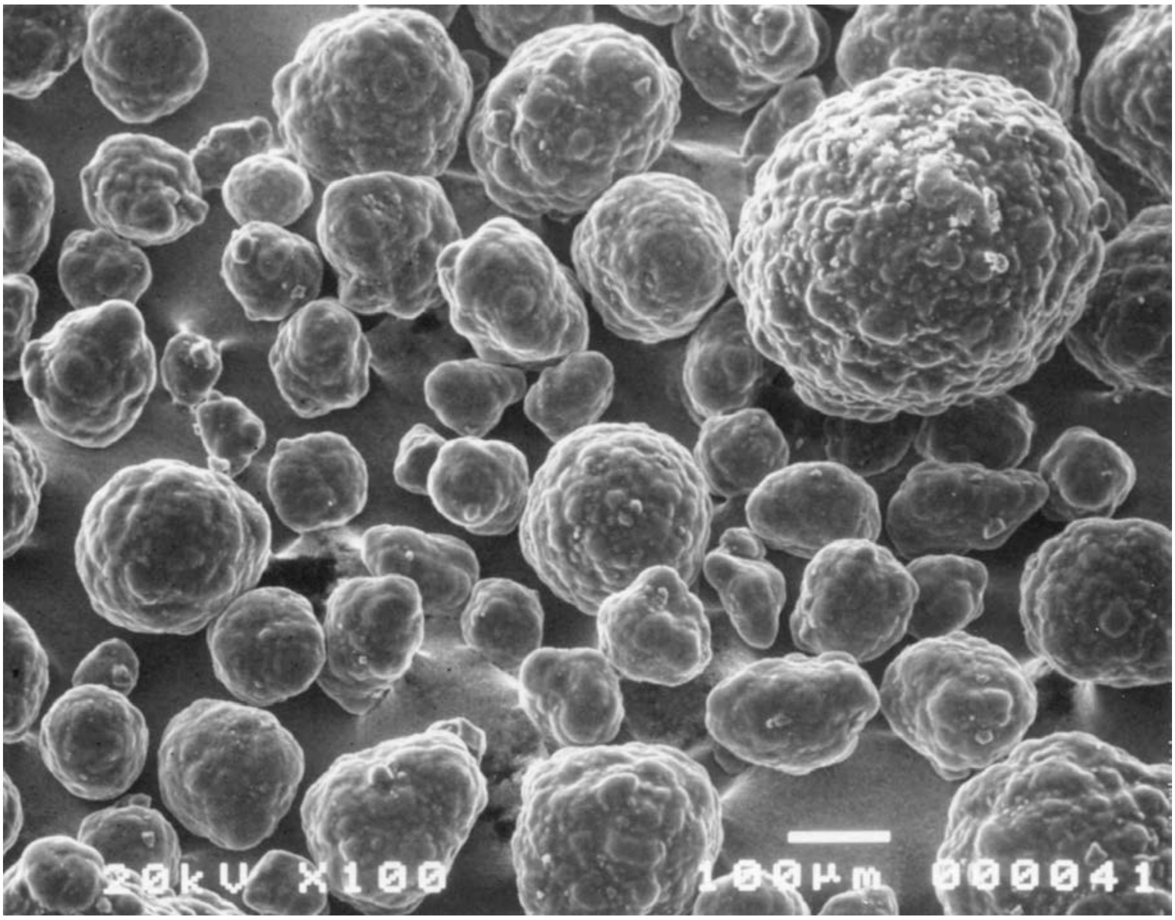

Figure 2.6 SEM of fluid coke *(Gray, 2002. Reproduced with permission of John Wiley & Sons, Inc. via Copyright Clearance Cente)*

The calculations, however, did not match with the experimental observations which showed a significantly thicker layer of coke in the end. This apparent contradiction can be explained by the fact that feed droplets managed to contact only a portion of the coke particles in the fluidized bed. In addition, thickness of coke layer deposits was found to be uniform across the coke particles. Random spraying of feed into a fluidized bed resulting in uniform coating on the surface of coke particles can be explained by studying the literature of granulation processes.

Granulation studies suggest that feed droplets, significantly bigger in size compared to the fluidized particles, tend to stick with multiple coke particles together. Increase in feed droplet size tends to increase the size of granules (Figure 2.7) (Waldie et al., 1991). The difference in fluid coking from other granulation processes arises in the fluidization velocities which are significantly higher in this case. Subsequently, granules tend to break due to shear forces in the bed unlike other processes where the granules are usually stable. The critical diameter for fluid coking is circa 70 μm (Dunlop et al., 1958). Therefore, when two particles each having a diameter of more than the critical value stick together, they eventually break apart to give separate particles with uniform coating of liquid (Figure 2.1). Alternatively, if one of the particles' diameters is less than 70 μm, then they remain together in the form of an agglomerate. The phenomenon is critical to understanding the mass transfer taking place in the reactor and its influence on product and coke yields.

Ali et al. (2014) found that reaction of vacuum residue in model agglomerates of coke particles with 8-12.5 wt% initial liquid content resulted in higher coke yield than in thin films of the same reactant. The difference was likely due to the retention of more cracked products in the liquid phase within solid-liquid agglomerates.

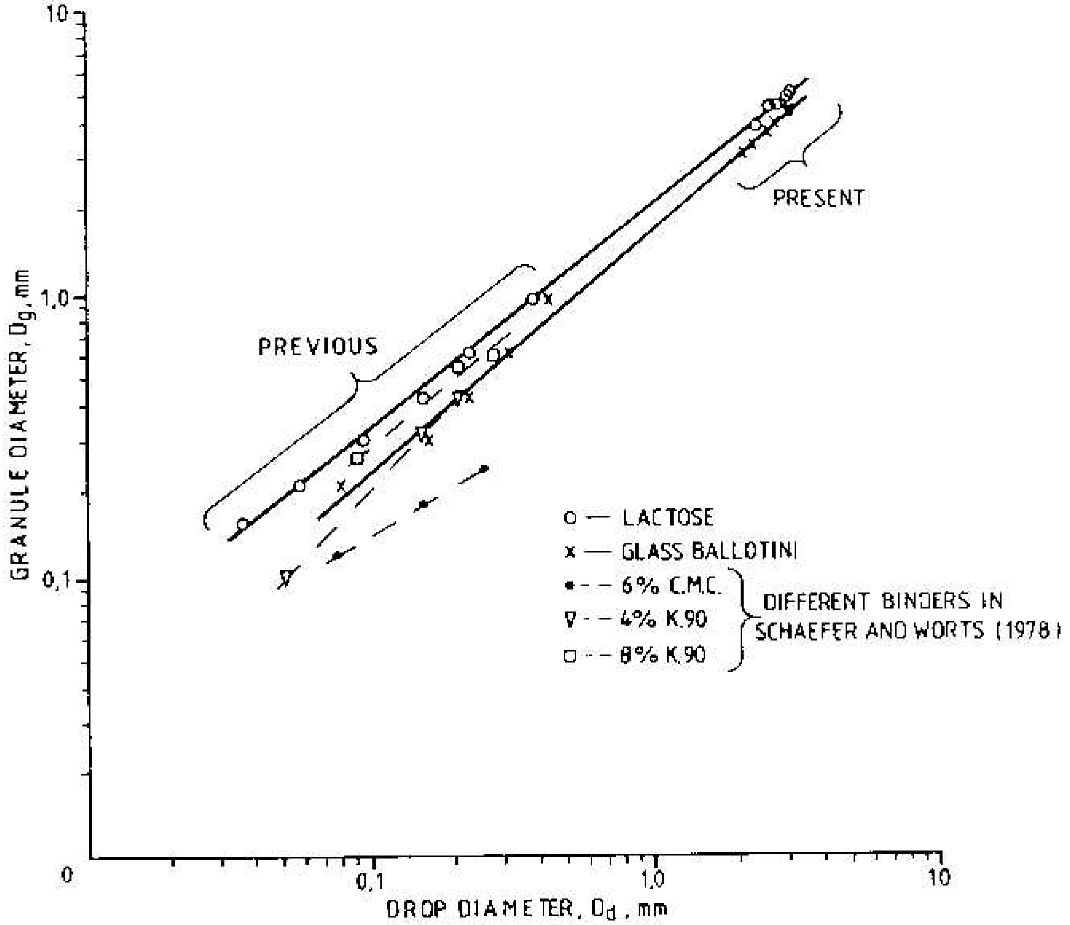

Figure 2.7 Relationship between the diameter of the feed droplet and the granule size. Increase in feed droplet size results in formation of granules of bigger size *(Reprinted from Waldie et al., Copyright 1991, with permission from Elsevier via Copyright Clearance Center)*

Coke yield in the model agglomerates was insensitive to initial liquid concentration, which in the study varied from 20% to 30% of liquid saturation in a packed pellet of coke particles. Higher liquid saturations, approximately ranging from 30 to 60%, would be expected to give an even greater distance for the cracked products to diffuse to the free liquid surface, and possibly to drive bubbling due to saturation of the liquid phase with volatile components. Increase in saturation levels above a certain limit, however, could lead to draining or bubbling off of liquid from the agglomerate due to the bubbling intensity, both of which would lead to redistribution of liquid feed, and consequently, a change in the liquid saturation of the agglomerates. Looking at the wet agglomerate in Figure 2.1, increase in path lengths for cracked products may be observed with increasing liquid content filling in the pores within the agglomerate. Liquid saturations may also extend to more than 100 % in theory but that would lead to the liquid draining off from the agglomerate leaving it with a lower liquid saturation.

Liquid distribution in a reactor is also related to the extent of fouling taking place. Some of the excess liquid draining off from agglomerates at very high saturations, or from particles impinging upon the walls of the reactors, may find its way onto the walls of the reactor resulting in formation of a liquid film on them. As the walls are impinged by more particles, liquid bridges are formed between the particles and the liquid film, eventually leading to formation of coke on these walls. The thickness of the liquid film on the wall determines whether the impinging particles will rebound after collision or coalesce with the film. Greater the thickness more will be the tendency to coalesce. The mechanism demonstrates the relation between fouling, liquid feed distribution in agglomerates and on the reactor walls, and the fluidization velocity in the bed which dictates the frequency of particles colliding with the walls of the reactor.

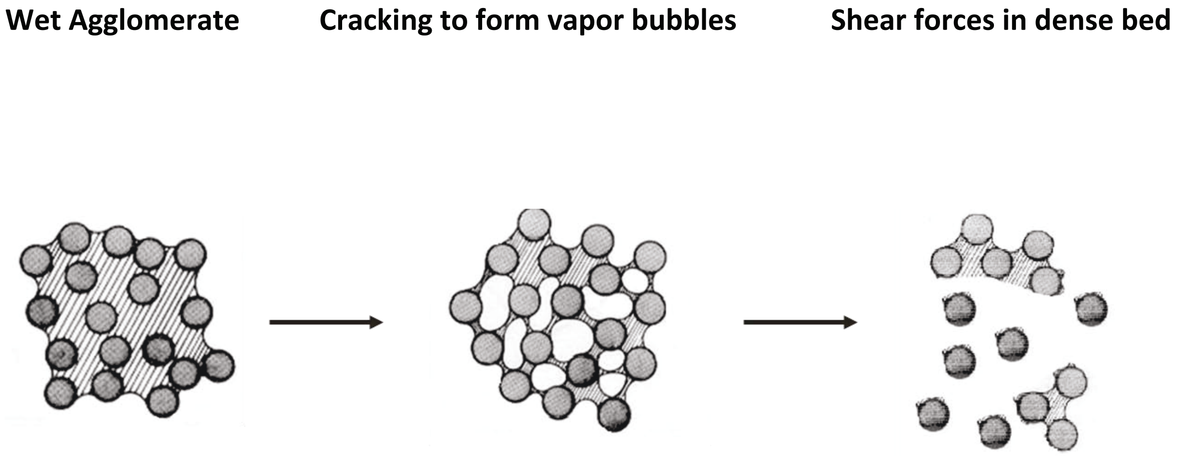

Figure 2.8 Stages of agglomerate formation and breakage are shown. Feed droplets interact with coke particles to form granules. Due to cracking in a fluidized bed and the subsequent shear forces, agglomerates undergo rupture in the final stage.

3. Materials and Methods

3.1 Materials

Three types of feeds derived from Athabasca bitumen were used in the experiments for preparing mixtures – Vacuum Tower Bottoms (VTB) from a commercial vacuum distillation operation, Vacuum Tower Bottoms 700+ (VTB 700+) prepared in the laboratory by short-path distillation, and unconverted material from a catalytic hydroconversion plant (LC Finer Bottoms). The data of Table 1 gives the properties of the feeds. All the feeds were supplied by Syncrude Canada Ltd. The microcarbon residue (MCR) content was determined by ASTM D-5430. The boiling curves were obtained from simulated distillation of feeds using ASTM D-7169. Fluid coke was also supplied by Syncrude. Its particle size was in the range of 100-200 μm.

Toluene came from Fisher Scientific (Missisauga, ON) and nitrogen from Praxair (Edmonton, AB), and were used as received. For heating the bitumen feed during mixture preparation, a beaker filled with thermo-oil (Sigma Aldrich, Silicone Oil, < 200°C) was used as an oil bath. Iron/Nickel alloy (Alloy 52) was supplied by Ametek Special Metals (Wallingford, CT) and were fabricated into special reactors at Karlsruhe Institute of Technology (KIT), Germany.

Table 3.1 Properties of bitumen-derived feed materials

Property	**Vacuum Topped Bottoms (VTB)**	**Short path vacuum residue (VTB 700+)**	**LC Finer Bottoms (700+)**
Density, kg/m^3	**1044**	**1106**	**1174**
Micro-carbon residue content (wt. %)	**22.4**	**33.4**	**56.4**
Vacuum residue content (524°C+), wt%	**85**	**100**	**100**
Fraction boiling over 650°C, wt%	**31**	**87.5**	**89.5**
Fraction boiling over 700°C, wt%	**13**	**75**	**71**
10% cut point, °C	**495**	**630**	**648**
Toluene insoluble solids, wt%	**1.6**	**3.4**	**11.2**

3.2 Bitumen Feed – Coke Mixture Preparation

To understand the role of liquid saturation on coke yield of agglomerates in fluid cokers, several coke-feed mixtures were prepared by mixing different ratios of feed and coke particles. For meaningful calculation of coke yield, it was necessary to have homogeneous mixtures which could be used in repeatable experimental runs without variation in its composition. A mixing setup was prepared for this purpose and the ratios prepared ranged from 12.5% to 23.5% weight percent of feed (30 to 60% liquid saturation). The mixtures prepared were then subsampled and analysed for composition to check for their homogeneity.

3.2.1 Mixing Setup

Bitumen feeds have high viscosities and do not mix well with other substances as a consequence, even if one does not take into the account the homogeneity which was required in the prepared mixtures. The feeds are solid at room temperatures and have to be heated to convert it into a fluid state. The mixing apparatus (Figure 3.1) consisted of a paint stirrer, which was modified for effectively distributing coke particles evenly in the liquid feed. A custom made stainless steel container was fabricated. The diameter of the container was made only slightly larger than that of the paint stirrer. This was done to ensure removal of mixtures from the inner wall of the container during the mixing process. The container, during mixing runs, was placed in an oil bath, which was essentially a beaker containing silicone oil. The oil bath, in turn, was placed over a hot plate (Fisher Scientific Isotemp). An oil bath was used instead of direct placement of the steel container over the hot place to ensure uniform heating all around the surface of the container instead of just heating at the bottom surface as a slight decrease in temperature along the curved surface walls was resulting in solidification of the feed, abruptly ending the mixing process. The oil bath was heated to a temperature of 160-200°C depending on the kind of feed being mixed with the coke particles. A magnetic stirrer was placed inside the oil bath to ensure faster heat transfer across the silicone oil medium. The temperature of the oil in the bath was controlled by dipping a thermocouple (K type) in the oil. Two metal bars were welded to the steel container to give it proper alignment while being placed inside the oil bath. The temperature was not raised above 200°C to prevent boiling of the lighter fractions of the liquid feed. The bars were mounted on stands to provide stability to the setup during fast rotation of the modified paint stirrer.

The stirrer was attached to a motor, the rotation speed of which could be regulated. The speed was varied depending on the mixture behaviour as some mixtures had a tendency to stick to the walls and not mix at higher speeds of rotation. The whole setup was placed inside a fume hood. About 200 g of mixture was prepared in one run. The coke and bitumen feed were weighed as per the ratio desired. Coke is a hygroscopic substance, and hence it was dried before its weighing (weighing machine - Mettler Toledeo AB104-S/Fact, least count – 0.1 mg). Drying took place in an oven where a large sample of coke was placed over a period of 30 minutes at a temperature of 120°C, followed by 15 minutes of cooling in a desiccator.

The feed was put first in the steel container which was exposed to heating and stirring for a period of 20 minutes to allow it to melt, followed by gradual addition of the coke particles. The setup was run for a period of 2 hours to ensure good mixing. The mixture was taken out after this and placed on a metal sheet to cool, which was kept in a freezer overnight at -16°C. The mixture was then manually crushed for 10 minutes using a metal pestle in a steel can. The resulting crushed particles were sieved into <1 mm particles and stored in the freezer for storage. Before usage, the powdered mixture was stirred with a spoon to get a uniform distribution in particle size for experimental usage.

Figure 3.1 Mixing Setup

3.2.2 Solids Content Analysis

The bitumen feeds were analysed for their solid content in order to determine the composition of the mixtures of coke prepared with the respective feeds on a solid free basis. Feeds were dried at 120°C for 10 minutes in a vacuum oven and then cooled for 10 minutes in a desiccator before they were weighed. This was done in order to remove any trace of moisture from the samples. Pure bitumen feeds are not hygroscopic like the coke particles or the mixtures prepared, but moisture may condense in the samples in the process of taking them out of the freezer for subsequent analysis. The weight of samples varied in the range of 140-200 mg. Filter paper (Millipore 0.22 μm type GVWP) was weighed and placed in the vacuum filtration setup shown in Figure 3.2. The samples were weighed by putting them in a weighed aluminium weighing dish. After placing it on the filter paper inside the vacuum filtration setup, the sample was rinsed with toluene repeatedly to ensure no soluble components remained on the filter paper. The toluene insolubles (solids present in the feed) were then taken along with the filter paper carefully, placed on aluminium weighing dish, which, in turn, was placed in a vacuum oven for period of 30 minutes for complete drying. The sample was then cooled in a desiccator for 10 minutes after which it was weighed. The respective weights of the samples, the filter membranes, and the aluminium weighing dishes were sufficient to calculate the solids content percentage in the feed as per the following calculation:

$$\boldsymbol{m_{feed} = m_{alu2} - m_{alu1}} \quad \textbf{(3.1)}$$

$$\boldsymbol{m_{solids} = m_{alu3} - m_{filter} - m_{alu4}} \quad \textbf{(3.2)}$$

$$\boldsymbol{x_{solids} = {}^{m_{solids}}/_{m_{feed}}} \quad \textbf{(3.3)}$$

Where m_{alu2} is the weight of the sample and aluminium weighing dish combination, m_{alu1} the weight of the aluminium dish, and m_{feed} the weight of the feed sample. m_{alu3} is weight of the summation of the aluminium dish (used for keeping the wet filter membrane after the filtration process), the filter membrane and the remaining toluene insolubles. m_{alu4} denotes the individual weight of the aforementioned aluminium weighing dish and m_{filter} the weight of the filter membrane. m_{solids} and x_{solids} represent the weight and the fraction of solids in the sample respectively.

This procedure was carried out five times for each bitumen feed sample. The mean of the experimental runs gave the final solids content of the respective feeds (Table 3.2).

Table 3.2 Solids content of bitumen feeds

Feed	Solids Content (weight %)	Standard Deviation (of five experimental runs)
Vacuum Topped Bottoms	1.64	0.18
Short path vacuum residue (VTB 700+)	3.39	0.27
LC Finer Bottoms	11.15	0.28

Figure 3.2 Vacuum Filtration Setup

3.2.3 Mixture Composition Analysis

The mixtures were subsampled and analysed to determine their compositions and their degree of homogeneity. A sample of about 140-200 mg was taken from the mixture and put into a weighed aluminium weighing dish. The dish was then placed in a vacuum oven for 10 minutes at a temperature of 120°C to remove any traces of moisture in the sample. The sample was then cooled in a desiccator for another 10 minutes before being weighed. Subsequently, the sample was slowly rinsed with toluene and poured onto a filter paper (Millipore 0.22 μm type GVWP), which was placed inside a vacuum filtration setup. The feed passed through the pores while the toluene insolubles remained at the end, which basically comprised the coke particles and the solids present in the feed. The filter membrane was placed in an aluminium dish and the whole setup was dried for a period of 30 minutes in the vacuum oven followed by 10 minutes of cooling in the desiccator before weighing it.

With the help of these weight measurements and fraction of solids content in the feed, fraction of feed in the mixture was calculated on a solid free basis. The ratio of toluene insolubles to the initial sample put for filtration was calculated in exactly the same manner as that of the solids content in the feed as discussed in the previous section. We refer to the toluene insolubles in this case as $m_{coke+solids}$, the initial sample which was put in the filtration setup as m_{mix}, and mass of feed excluding solids as $m_{feedsolidsfree}$. To determine the fraction of feed in the mixture on a solid free basis, the following equations were solved simultaneously.

$$\boldsymbol{m_{feedsolidsfree} = m_{mix} - m_{coke+solids}} \qquad \textbf{(3.4)}$$

$$m_{feed} * (1 - x_{solids}) = m_{feedsolidfree} \tag{3.5}$$

$$m_{solids} = x_{solids} * m_{feed} \tag{3.6}$$

$$x_{feedsolidsfree} = {}^{m_{feedsolidsfree}}/_{(m_{mix} - m_{solids})} \tag{3.7}$$

Five experimental runs were done per sample and the mean gave the percentage compositions. The composition of the mixture is shown in Table 3.2.

Table 3.3 Composition of mixtures prepared

	Vacuum Topped Bottoms	Short path vacuum residue (VTB 700+)	LC Finer Bottoms
Percentage composition of feed in the mixture (solid free basis)	12.7 ± 0.4	15.8 ± 0.8	17.5 ± 0.5
	16.4 ± 0.3	20.3 ± 0.3	24.1 ± 0.1
	19.5 ± 0.1		
	22.2 ± 0.3		

3.3 Coking Experiments

3.3.1 Induction Furnace

Following previous work (Gray et al., 2001; Gray et al., 2004; Ali et al., 2010), samples were rapidly heated in a nitrogen atmosphere using an induction furnace. The overall apparatus is illustrated schematically in Figure 3.3. An induction furnace (Ameritherm Inc., Induction Furnace Model XP-30, Scottsville) was used to provide a high heating rate to specially designed reactors fabricated out of Alloy 52, which is discussed in detail in the next section. The reactors were placed on a ceramic holder inside a Pyrex glass pipe passing through the induction coil. The pipe was sealed with flanges at each end, and purged with nitrogen gas to provide an inert environment for the reaction and to sweep reacted products away from the hot surfaces. The product gases were taken out through an air filter and into a fume hood. The weight of the remaining coke at the end of experiments was measured at the end of each experimental run. Use of induction furnace was extremely beneficial to the project goals in terms of the conditions it created, which were similar to conditions prevalent in the fluid coking reactors. It provided for extremely high heating rates (around 110°C/sec at full power) and gave an excellent control over final reaction temperature due to the unique property of induction heating which allowed for heating of only magnetic substances. Thus, by using Curie point alloys, magnetism of which were lost at their Curie point temperatures, it became possible to control the temperature till which heating was to be done simply by choosing the alloy with the desired Curie temperature.

The heating rate in the induction furnace was controlled by varying the voltage in the setup. At the highest voltage setting, the heating rate was as fast as 110°C. And the lowest setting corresponded to a heating rate of 15°C/sec. A water tank was used to pass water through the coils during the heating process to insulate it from the heating due to the intense magnetic fields generated.

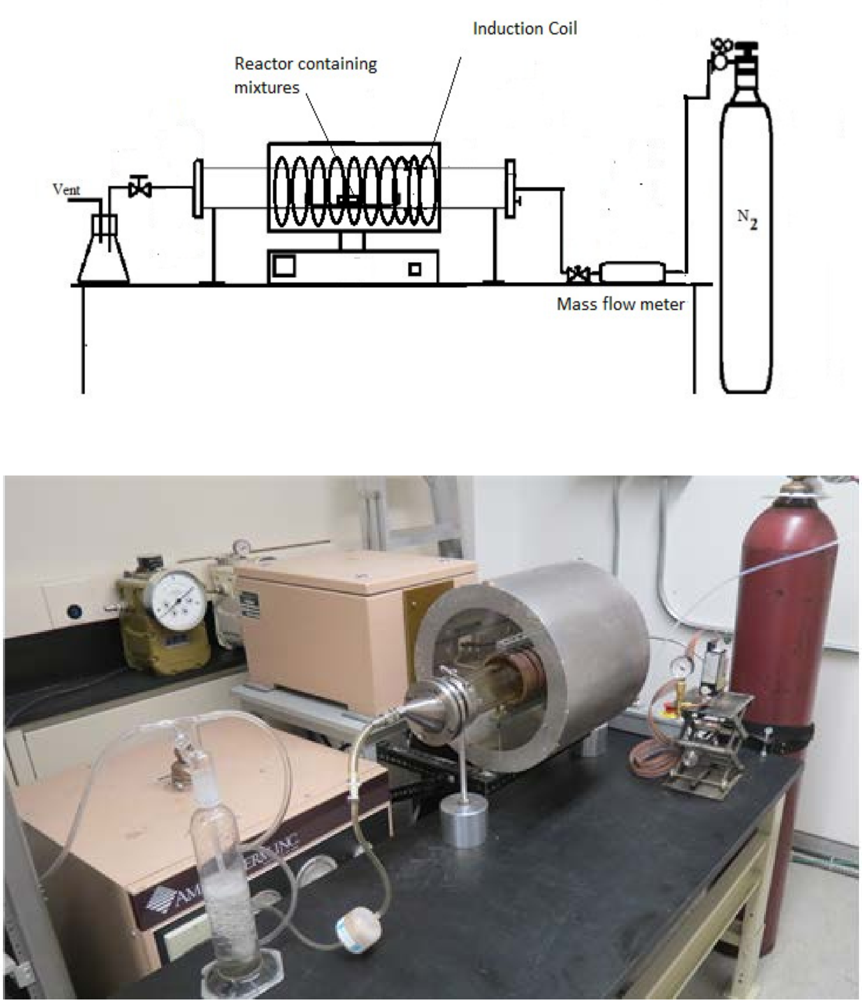

Figure 3.3 a, b a) (top) Schematic of the experimental setup consisting of an induction furnace and reactor placed inside the Pyrex glass pipe passing through the induction coil; b) (bottom) Photograph of the experimental setup

3.3.2 Reactors

Specially designed Curie point reactors were used as a source of heat for cracking the mixtures. The reactors were fabricated out of Alloy 52 (alloy of nickel and iron) which has a Curie temperature of 530°C. So by using this alloy, the final temperature reached 530°C in the furnace after which there was no further increase in temperature. This scenario was an excellent fit for the experiments since the final reaction temperatures in a fluid coker are in the range of 500 to 550°C. All the reactors were fabricated at Karlsruhe Institute of Technology (KIT), Germany under the supervision of Dr. Peter Pfeifer. The mixtures were put inside the reactors and then the reactors were placed inside the furnace. It is important to note that heating of mixtures was due to conduction of heat from the rapidly heating Alloy 52 reactors, and not because of induction heating of the mixtures, simply because coke-bitumen feed mixtures are non-magnetic in nature and would be resistant to any attempt of induction heating. Different designs of reactors were used for testing different objectives. The designs are described in the following sections.

3.3.2.1 Reactor I

Reactor I was fabricated out of thin strips of Alloy 52 and a well was carved out in it, inside which the mixtures were placed during the experimental runs (Figure 3.4). The thickness of Reactor I depended on the well depth desired, and it was varied by laser welding thin strips of Alloy 52 together. A well depth of 1.2 mm was used for the majority of the runs and referred to as Reactor Ia. Two other well depths were used to compare the coke yield with varying depths. They were 2 and 0.6 mm in depth and were referred to as Reactor Ib and Reactor Ic. The ratio of the depth to the diameter was small; therefore, mixtures of coke and reacting feed in the wells approximated a 1-dimensional reactor, with heat applied at one end and a free surface to enable the escape of vapors at the other end. The well design allowed rapid heating and the use of high liquid saturations without gravity drainage from the solid-liquid mixture.

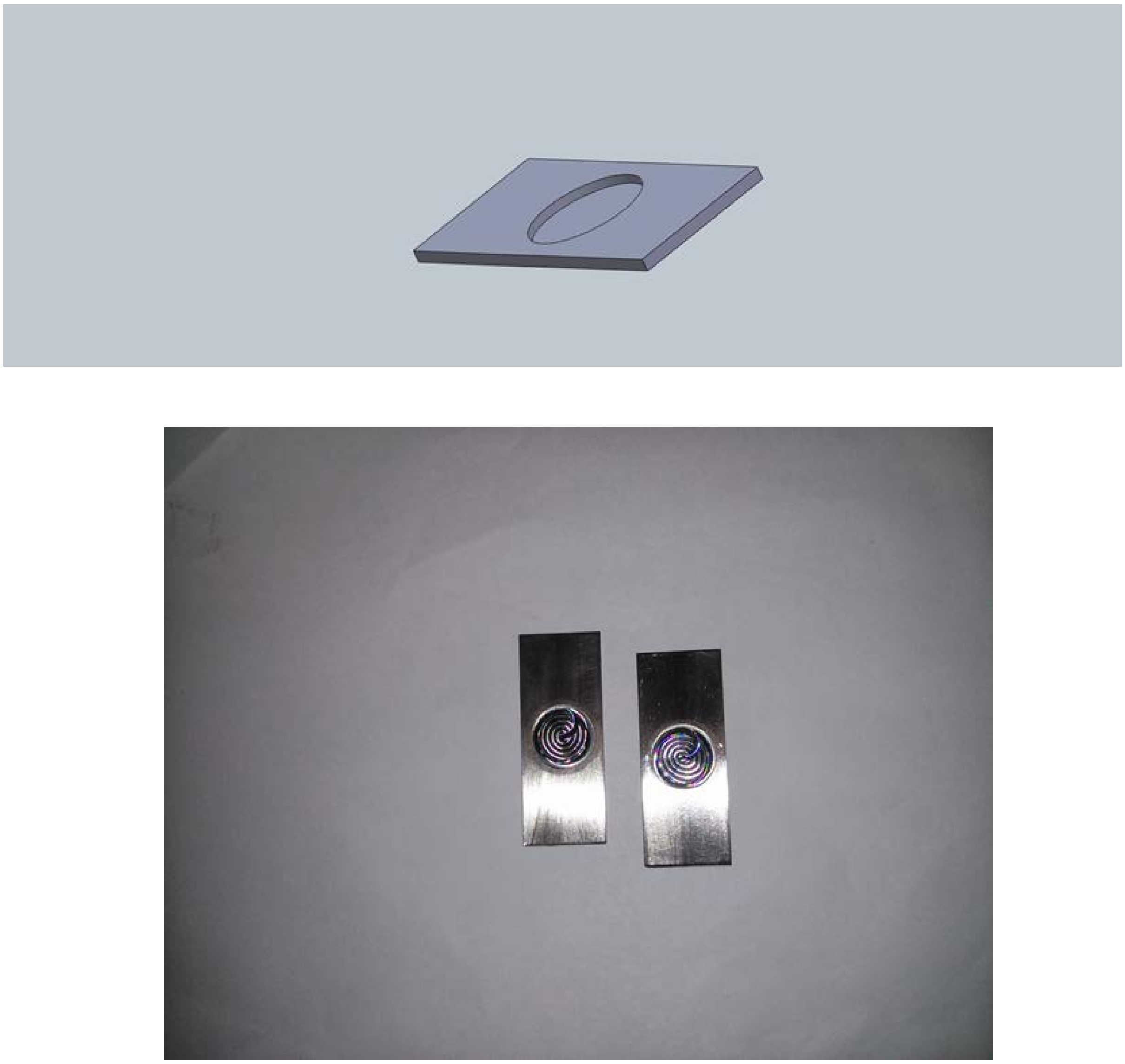

Figure 3.4 a, b a) (top) Diagram of Reactor I made of Iron/Nickel Alloy (Alloy 52) with a well for mixtures of reacting liquid and solid coke particles. The well depths were 0.6 mm, 1.2 mm or 2 mm, and the well diameter was 15 mm in all cases; b) (bottom) Top view of Reactor I.

3.3.2.2 Reactor II

Reactor II was again made out of Alloy 52 strips, however with a different geometry, the purpose of which was to give excellent control of diffusion path lengths to study the impact of those on the yield of coke in the reactions. Channels with a width of 100 microns were machined into the strip (Figure 3.5). The channels were cut right through the metal strip meaning the depth of the channels were the same as the height of the strips, i.e., 1.2 mm. The feed was loaded into the channels and were held in place because of the capillary forces. An important distinction in this reactor compared with Reactor I was in the fact that pure feeds were used during loading instead of coke-feed mixtures as used earlier. Not only was it impractical to load a homogenous coke-feed mixture into these extremely thin channels, there was no reason to do so. The coke particles in coke-feed mixtures were being used to heat the feed similar to the hot coke particles heating feed droplets in fluid coking reactors. The primary objective in that case was to examine the effect of liquid saturation of coke-feed mixtures on the cracking chemistry which could indirectly be related to diffusion path lengths. Reactor II's primary objective, meanwhile, was to look at direct coke yield dependence on path length of diffusion. The rapid heating in this case was to be provided to the feed within the micro channels solely by the metal. Reactor II had 2-dimensional geometry with rapid heating taking place from both sides in contrast to the bottom surface heating taking place in Reactor I.

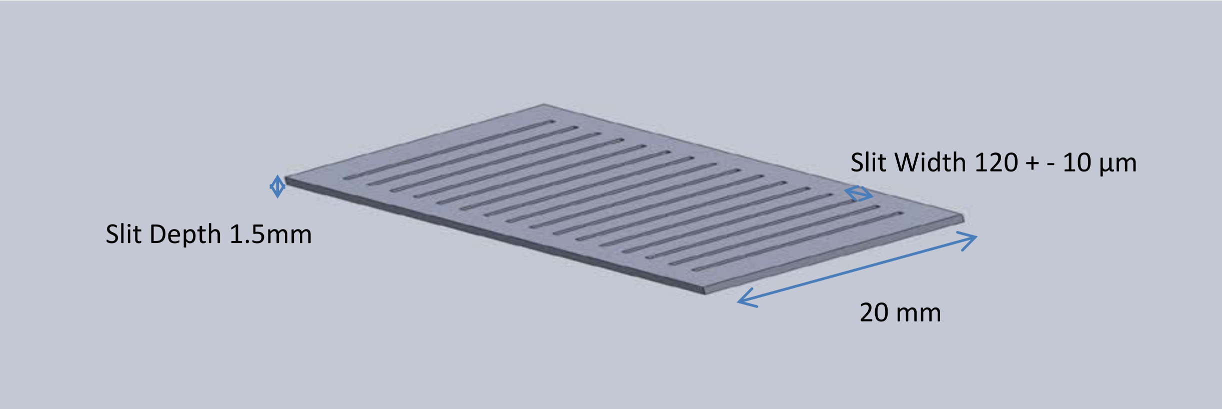

Figure 3.5 Sketch of Reactor II made out of Alloy 52 with micro channels machined into it for reacting liquid feeds

3.3.2.3 Reactor III

Reactor III was essentially a combination of Reactor I and Reactor II. The goal of this reactor was to check for the formation of coke on the surface of the mixture while the interior of the mixture was still liquid, and if that had an impact on the coke yield of the mixtures because of potential trapping of liquid and vapor inside the mixture. Rapid heating along the surface of an agglomerate might help in formation of a surface layer of coke or a “skin” due to the differential heating within the agglomerate. Reactor III configuration was used to provide heating on the surface to simulate the differential heating. Reactor III was made by capping Reactor I with Reactor II (Figure 3.6). The mixtures were kept in the well of the Reactor I, and Reactor II was placed on top of it to allow for heating from the top. The channels in Reactor II provided an escape route for cracked product gases. Reactors Ia and Ib were used for making this configuration to give Reactor IIIa and IIIb respectively.

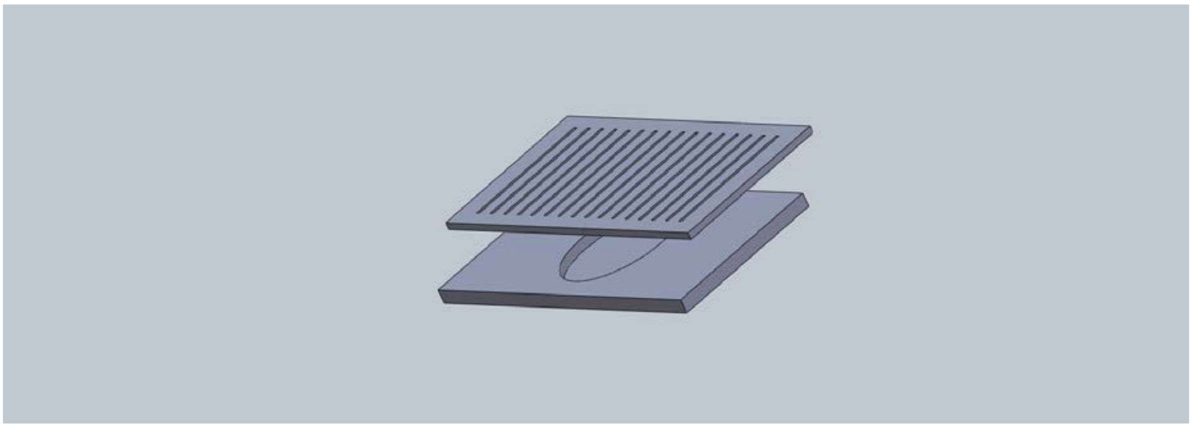

Figure 3.6 Sketch of Reactor III made of a combination of Reactor I and Reactor II. Mixture is placed in Reactor I and capped by Reactor II. The channels in Reactor II allow for escape of product vapors

3.3.3 Reaction Procedure

3.3.3.1 Loading of Reactor I and Reactor III

The loading process for Reactor I and Reactor III was the same, except for the fact that the orientation of Reactor III on the ceramic holder was slightly different from that of Reactor I explained later in this section. After noting the weight of the reactor, a sample of feed-coke mixture was placed in the reactor well. The reactor was then placed in a vacuum oven at a temperature of 120°C for 10 minutes to remove the moisture that had been absorbed by the hygroscopic coke particles, and then allowed to cool in a desiccator for another 10 minutes. After weighing the reactor plus mixture sample, it was placed on a ceramic holder and put inside the glass pipe of the apparatus. While in case of Reactor I, it was placed on the bottom surface of the ceramic holder as shown in Figure 3.7a, Reactor III's ends were placed on the holder's raised edges in a configuration similar to what is shown in Figure 3.7b in order to prevent the bulk of the surface of the reactor in making actual contact with the ceramic holder. This was done because the escape of cracked products was not as efficient as in the case of Reactor I due to less surface area available for their escape. Small amounts of cracked gases were observed to be condensing on the relatively cooler ceramic surface and trickling down to the reactor, when Reactor III was placed in Reactor I configuration (Figure 3.7a), making the weight measurements non consequential. Placing Reactor III in the manner mentioned above, and as shown in Figure 3.7b, mitigated this problem.

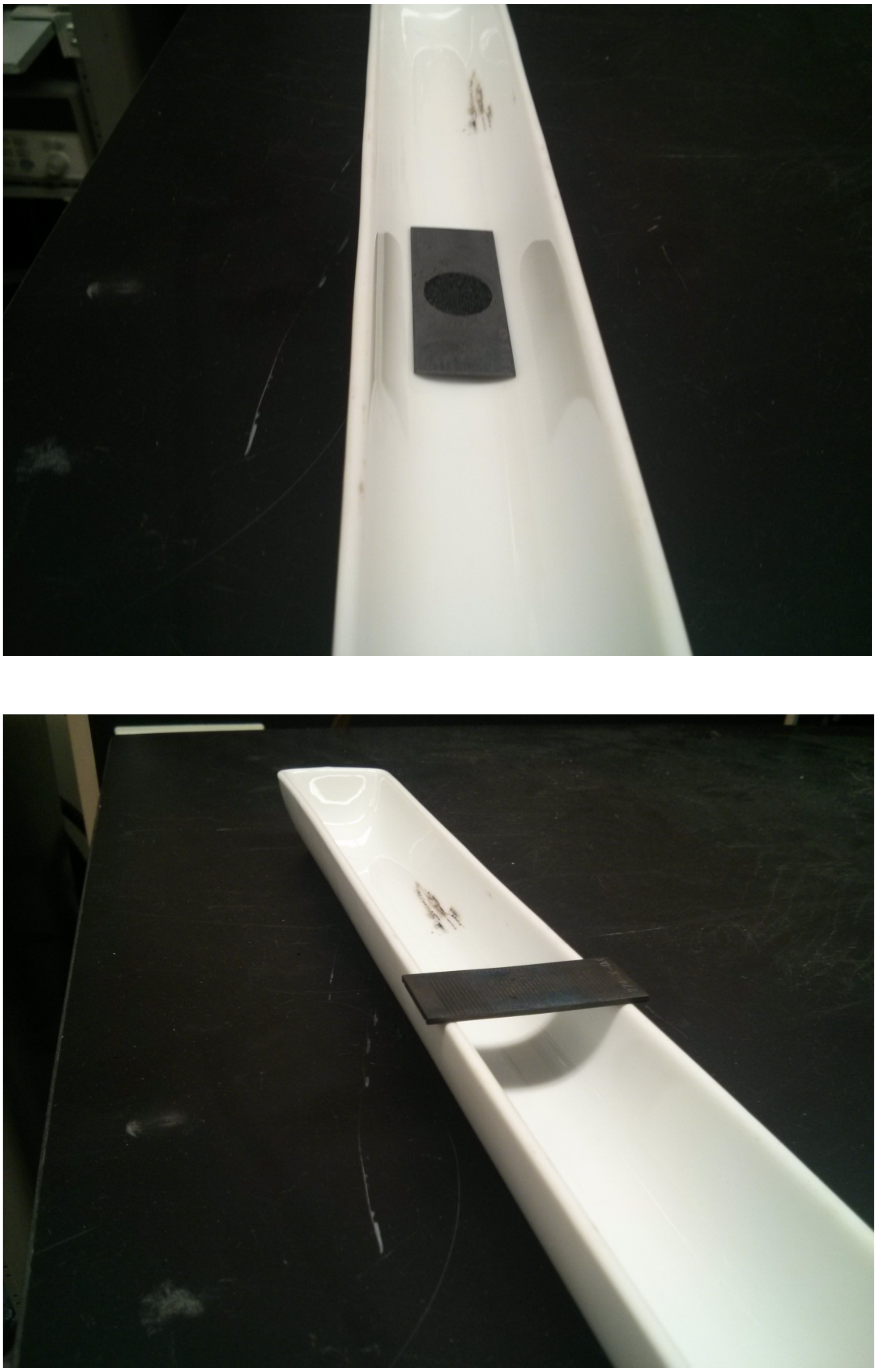

Figure 3.7 a,b a) (top) Reactor placed on the edges of the ceramic holder; b) (bottom) Reactor placed on the bottom surface of the ceramic holder

3.3.3.2 Loading of Reactor II

Loading of Reactor II was more complicated than the other two reactors due to the presence of the micro channels, and usage of pure bitumen feeds which are solid chunks at room temperature. Hence, the feed to be loaded was first heated in oil bath to a temperature of 160-200°C depending on the kind of feed, to reduce its viscosity and make it fluid. Reactor II was then dipped into the container to allow for the feed to enter the channels and kept in the container for a period of 5 minutes. The reactor was taken out quickly at the end of this period and wiped off to remove feed coating on the external surface of the reactor before the feed cooled down. Complete removal of feed deposited on the surface was done by careful wiping of the surface with a paper wipe dipped in toluene. The whole process ensured a loading of feed into the channels, and not on the surfaces of the reactor. The reactor was then dried in an oven for 10 minutes at 120°C to dry off traces of toluene. It was subsequently cooled down by placing it in a desiccator for another 10 minutes. The weight was taken and then this reactor was placed on the ceramic holder in the same way as Reactor III, i.e., on the raised edges to ensure minimum contact with the surface of the holder. This was done for precisely the same reason as in the case of Reactor III, which was to avoid condensing of cracked gases around the reactor.

3.3.3.3 Operation of Induction Furnace

3.3.3.3.1 Coke Yield Runs

In the experimental runs across all reactors, the loaded reactors were placed on a ceramic holder in the described configuration and put inside the glass pipe of the apparatus. The apparatus was closed and purged with nitrogen at a flow rate of 5 L/min at atmospheric pressure for 10 minutes after which the induction furnace was turned on. The reaction was allowed to proceed for 5 minutes which was more than sufficient to ensure complete coking to take place in the reactor. Alloy 52 has a Curie point of 530°C, which allowed the reactor to heat to this temperature within the induction furnace. At the end of the reaction time, the reactor was cooled down inside the pipe for 10 minutes in an atmosphere of nitrogen, then transferred to a desiccator for 10 minutes before weighing. The mass yield of coke was calculated as follows:

$$Coke\ yield, \% = \frac{m_{product\ coke}}{m_{feed}(1-w_{TI})} x100 = \frac{m_{final\ sample} - m_{initial\ sample}(1-w_{feed})}{m_{initial\ sample} w_{feed}(1-w_{TI})} x100 \quad (3.8)$$

Where *m* is mass as indicated, w_{TI} is the weight fraction of toluene insoluble material in the feed (Table 3.2) and w_{feed} is the weight fraction of feed in the mixture sample.

The heating rate to reach the final reaction temperature of 530°C was controlled using the voltage control of the induction furnace. The actual temperature of the reactor was measured by spot welding a thermocouple wire to make a junction on the reactor. The highest heating rate for the experimental runs was approximately 110°C/sec while the slowest heating rate was 15 °C/sec.

3.3.3.3.2. Bubbling Runs

The bubbling runs were done to observe bubbling in the mixtures. The process of loading was the same as that in coke yield runs, except that reactors were not weighed in this case as the runs were purely observational in nature. The induction furnace was run with different heating rates starting from approximately 15°C/sec to 110°C/sec for a period of just two minutes to check the formation and intensity of bubbling taking place as almost all of the bubbling took place within 30 seconds from the start of the reaction. Bubbles were observed by eye with the help of powerful lighting. Videos of bubbling were also recorded.

4. Results and Discussion

4.1 Cracking of Mixtures in Reactor I

4.1.1 Coke Yield from VTB-Coke Mixtures

Four mixtures with VTB concentrations from 12.7 to 22.2 wt% (Table 3.2) were tested with Reactor Ia. The coke yield for each run was calculated by overall mass balance (equation 3.8), and the results are shown in Figure 4.1. A total of 18 repeat experiments were done for each feed concentration to check the repeatability, and the mean and confidence interval calculated for each mixture. A definite trend was observed, with the coke yield increasing with increase in liquid concentration (Figure 4.1). The coke yield ranged from 7.8 ± 1.8% for the 12.7% mixture to 12.9 ± 0.9% for the mixture having the highest liquid concentration of 22.2 wt% by VTB. Each increment in concentration above 12.7 wt% gave a statistically significant increase in coke yield, based on two tailed t-tests with 95% confidence.

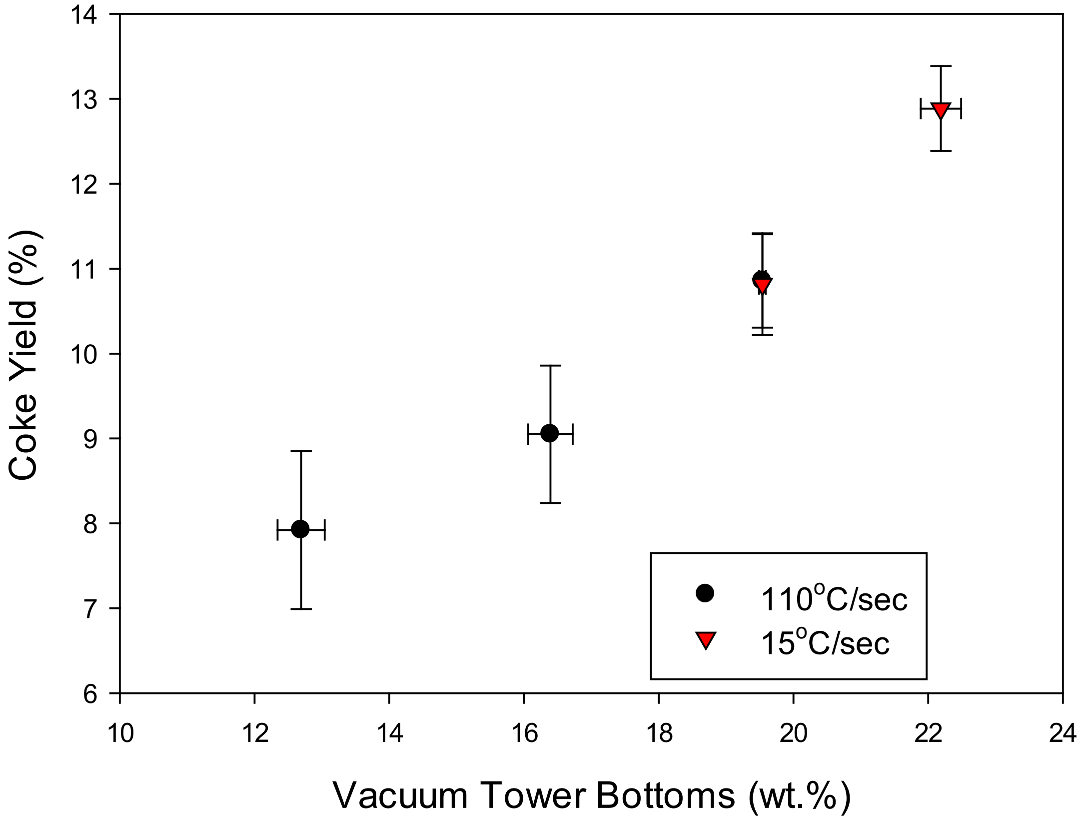

Figure 4.1 Effect of concentration of VTB on coke yield at high and low heating rates. Error bars represent the 95 % confidence interval from replicate experiments (*n*=18) for actual mixture concentrations (x-axis error bars) and coke yields (y-axis error bars) respectively.

When a heating rate of about 110°C/sec was used for the mixtures with 12.7 and 16.4 wt% VTB, no bubbling was observed in the reactor well during the experiment. Slight bubbling was observed in the 19.5 wt% mixture, and for the 22.2 wt% mixture the bubbling was severe so that significant liquid escaped the well. When the heating rate was lowered to about 15°C/sec, no bubbling was observed for the 19.5 wt% mixture, and the intensity of the bubbling for the 22 wt% mixture was reduced so that the liquid remained in the reactor well. The coke yields from these lower heating rates are shown in Figure 4.1. For the mixture with 19.5 wt% feed, the coke yield was insensitive to the presence of bubbling because there was no significant difference between the two results. Given the lack of sensitivity of the coke yield to bubbling, so long as the liquid was retained, the data for the 22.2 wt% mixture are shown on the same plot, and appear to continue a consistent trend. Mixtures with VTB concentrations of more than that 22.2% showed very high intensity of bubbling at all heating rates, leading to spillover and loss of sample. Consequently, 22.2 wt% was the highest concentration of liquid possible with this experimental method.

The reason for the increase in coke yield with weight fraction of liquid is likely due to increased diffusion path lengths in the reacting liquid phase. Higher weight fractions mean higher liquid saturation, which is the degree of liquid filling the void spaces in the mixture. Higher liquid saturations would reduce the void space for vapor, and give thicker liquid films and liquid-filled pores between the coke particles. This increase in diffusion length of cracked products in the reacting liquid phase would increase the rate of trapping, thereby increasing the final yield of coke. At still higher saturation levels, however, liquid could drain off from the agglomerate or bubble off due to the bubbling intensity, both of which would lead to redistribution of liquid feed, and consequently, a change in the liquid saturation of the agglomerates. The results of these experiments are consistent with the findings from studies with controlled liquid film geometry, that thicker liquid films lead to higher coke yields (Dutta et al., 2001; Gray et al., 2001; Radmanesh et al., 2008).

Ali et al. (2010), however, deviate from this trend. The coke yield measured in those experiments was insensitive to increase in weight fraction of liquid and consequently the liquid saturation in 3 mm agglomerates (Figure 4.2). Not only was there no observable trend in between the data points corresponding to different liquid saturations in the 3 mm agglomerates, the coke production factor (coke yield at experimental conditions divided the MCR content of the particular feed) was found to be significantly larger than those measured from Reactor Ia runs despite lower weight fractions or the consequent liquid saturations. A possible explanation for this contradiction can be explained by looking at the thickness of mixture tested. Well depth of Reactor Ia was 1.2 mm, a smaller value compared to 3 mm agglomerates used in the experiments done by Ali et al. (2010). A larger thickness sandwiched between Curie point strips providing heating at the surface could have led to formation of skin due to differential heating between surface of the agglomerate and its interior. A skin forming on the surface can potentially prevent escape of product vapors from the agglomerate, leading to the higher coke yields presented in Figure 4.2. The lack of trend within the coke production factor from different weight fractions of liquid, could probably be because of the large variation in coke production factors (denoted by large error bars in Figure 4.2) within replicate experiments for each weight fraction of the liquid and the resulting liquid saturation of agglomerates prepared by Ali et al. (2010). The variation could be due to lack of repeatability in the skin formation process.

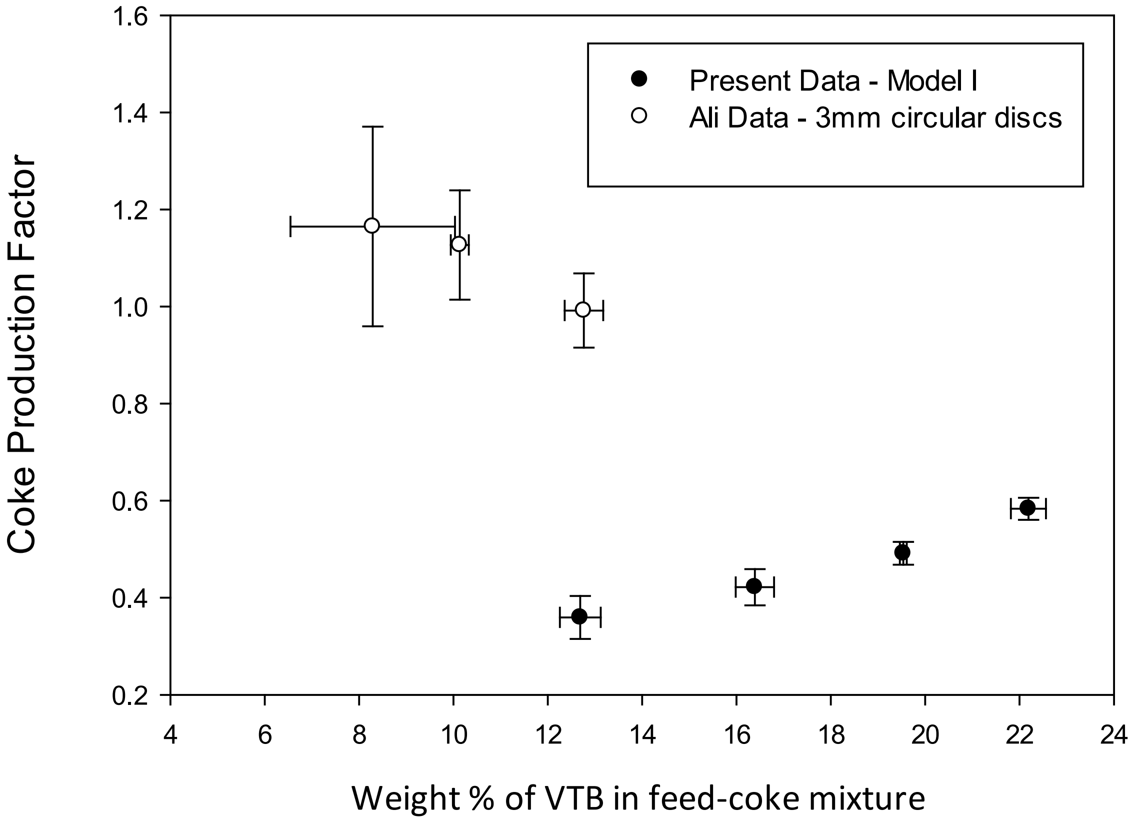

Figure 4.2 Comparison between coke production factors of experiments done by Ali et al. (2010) for 3 mm agglomerates and those obtained from Reactor 1a runs of concentration of feed. Error bars in *x*-axis and y-axis represent the 95 % confidence interval from replicate experiments (n=18) for Reactor Ia and n=8 for data from Ali et al. (2010)) for finding actual mixture concentration and coke yields respectively.

4.1.2 Effect of Heating Rate on Bubbling and Coke Yield

In order to examine the impact of heating rates used to reach the final reaction temperature of 530°C in the cracking experiments, additional experiments were conducted with VTB-coke mixtures, with heating rates of about 110°C/sec and 15°C/sec. Figure 4.3. shows the coke yields from two different mixtures, having 16.4% and 19.5% by weight of VTB. The ultimate coke yields were insensitive to heating rates when the reaction time at a constant final temperature (530°C) is long enough for the cracking to be complete. This finding is consistent with the results of Ali et al. (2010), who showed that coke yields from thin films did not show a dependence on heating rates.

Bubbling was not observed in the 16.4% mixture even at the high heating rate. The 19.4% VTB coke mixture was observed to be the transition concentration, where the reacting mixture went from a non-bubbling to a bubbling regime. Bubbling was consistently found to occur at a heating rate of approximately 110°C/sec in this mixture while being absent at the slow rate of around 15°C/sec. At higher liquid concentrations, bubbling could not be prevented from occurring even at the lowest heating rate. So bubbling was found to increasing with both heating rate and liquid concentration. The effect of bubbling on coke yields at transitional concentrations was not significant as shown in Figure 4.1 and 4.3.

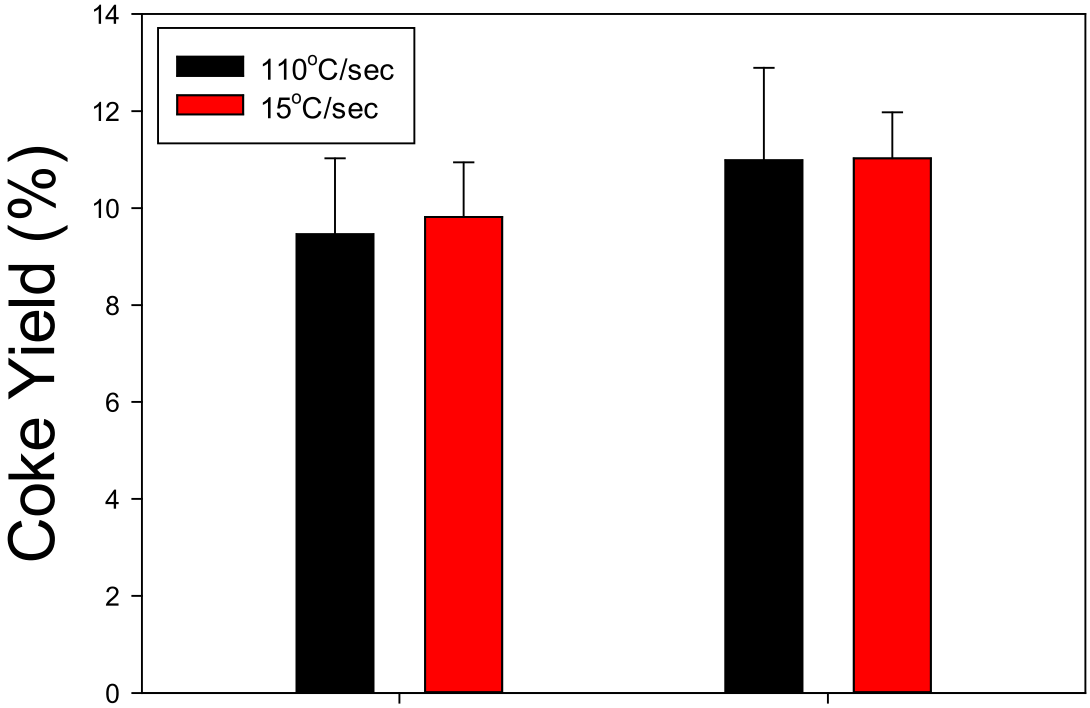

Figure 4.3 Effect of heating rate on coke yield of VTB coke mixtures having concentrations of 16.4% and 19.5% by weight of VTB respectively. Error bars in y-axis represent the 95 % confidence interval from replicate experiments for finding coke yields (n=12).

4.1.3 Effect of Well Depth on Coke Yield

Reactors Ia, Ib, and Ic, corresponding to well depths of 1.2 mm, 2 mm, and 0.6 mm respectively were used for this set of experiments. 16.4% VTB coke mixture was reacted in the reactors to check for the dependence of coke yield on the thickness of the layer of the reacting mixture. This specific concentration was selected for the experiments because it did not give any bubbling. As illustrated in Figure 4.4, the difference in the ultimate coke yield was statistically insignificant for the relatively narrow range from 0.6 to 2 mm, consistent with Ali et al. (2010) who had shown that coke yield was insensitive to agglomerate thicknesses in the range of 2 mm to 4 mm. This result is consistent with the mechanism discussed earlier, because 16.4 wt% VTB corresponds to liquid filling 38% of the pore volume. Once products escaped the liquid phase, they would flow through the vapor space within the pore volume, and this flow would be unaffected by a change of path length from 0.6 to 2 mm.

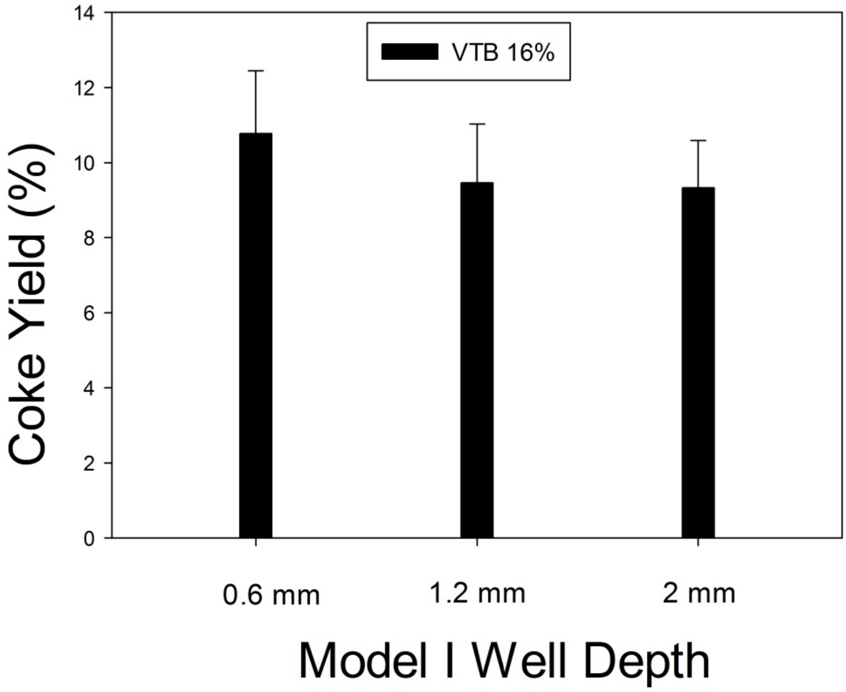

Figure 4.4 Effect of well depth on coke yield of 16.4% VTB coke mixture. Error bars in y-axis represent the 95 % confidence interval from replicate experiments for finding coke yields (n=8).

4.1.4 Coke Yield from Different Feeds

Equivalent experiments were conducted with LC Finer Bottoms and VTB 700+ feed stocks. These feeds gave different concentrations of very high boiling components and different yields of coke from the standard MCR determination (ASTM – D5430). The feeds were tested for their solids content in order for all the results to be reported on a solid free basis. LC Finer bottoms had a relatively high solid content of 11.2% by weight of feed compared to 1.6% and 3.4% of VTB and VTB 700+ respectively. To effectively compare the feeds, the coke yields were standardised to coke production factors, which, as stated earlier, is the yield of coke at the experimental condition divided by the MCR content (Table 3.1.). A plot of coke production factor versus liquid concentration of feed in the mixtures (Figure 4.5), shows that all three feeds gave a trend of increasing coke yield with increase in liquid concentration of the mixtures. The coke production factor from LC Finer Bottoms was found to be the highest and VTB 700+ to be the lowest.

All of the coke production factors were below 1.0, which means that more of the sample mass escaped as vapour product in these experiments than in the ASTM apparatus. Although some of the cracked products were likely trapped in the agglomerates due to mass transfer limitations, as discussed above, the tubes used in the ASTM test give higher coke yield because they condense and recycle some of the “lighter” residue components into the heated zone. Consequently, any apparatus that minimizes such recycle, such as thin films (Gray, 2002) or modified gas flow in the ASTM device (Wiehe, 2008) will give lower coke yields than the ASTM D-5430 test. Normalizing the coke yields from different feeds using the respective MCR contents should mean the difference in coke yields that could arise due to difference in the properties of feeds disappear in the plot (Figure 4.5), and the three curves should superimpose.

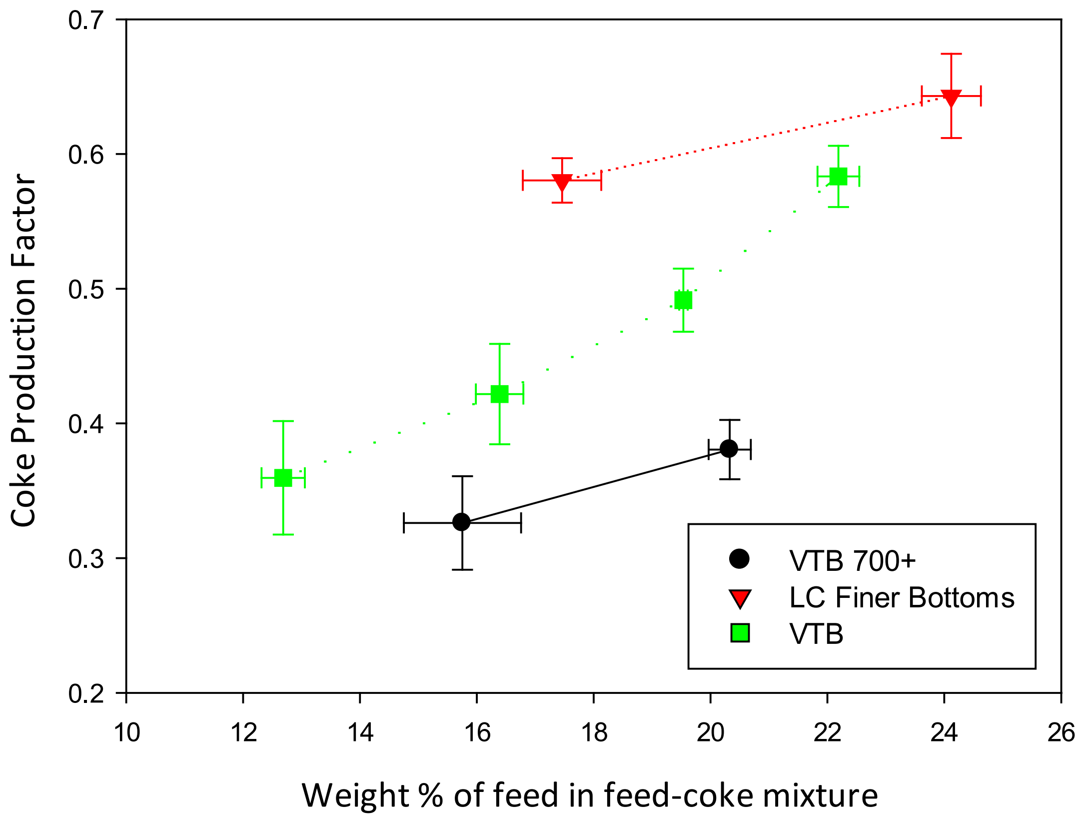

Figure 4.5 Effect of concentration of VTB, VTB 700+, and LC Finer on coke production factor. Error bars in *x*-axis and y-axis represent the 95 % confidence interval from replicate experiments for finding actual mixture concentrations and coke yields respectively.

The curve of VTB being significantly above that of VTB 700+ is an interesting finding. VTB has lower boiling point fractions than VTB 700+ (Table 3.1), lower density as well as lower viscosity. Although this order of curves (Figure 4.5) should not be confused with coke yields from these feeds which were still highest in LC Finer Bottoms and lowest in VTB in line with their MCR values. Figure 4.5 suggests that the coke production factors (cpf) for both the heavier feeds, i.e., LC Finer Bottoms and VTB 700+ show less sensitivity with variation in wt fraction of the liquid in the mixture. This could be due to less vaporization and higher viscosity of these feeds in the liquid phase. Consequently, with increase in wt fraction of liquid in the mixture, the cpf of VTB is observed to more than that of VTB 700+, and addition of lighter components to VTB 700+ would lead to higher cpf at higher liquid wt fractions in the range shown in Figure 4.5. LC Finer Bottoms, despite its low sensitivity towards liquid wt fractions, has higher cpfs. One of the reasons for this occurrence is that LC Finer Bottoms is chemically different from VTB and VTB 700+, with most of the easily cracked products removed from this feed.

Difference in solids content among the feeds is not a major factor for these experiments as toluene-insoluble solids can give a transient suppression of coke formation (Tanabe and Gray, 1997) but have little impact on coke yields at high severity.

4.2 Cracking of Feeds in Reactor II

Two feeds, VTB and VTB 700+, were reacted in Reactor II. Just feeds, and not mixtures of coke and feeds, were tested for coke yield as discussed in detail in Section 3.3.3.2. To reiterate, the aim of the reactor was to check the dependence of coke yield on diffusion path length (half of the channel depth, i.e., 600 μm). In the experimental runs, it was observed, however, that coke had got deposited on the surface of Reactor II on both sides rather than remaining within the micro channels in the reactor. The rapid heating of the feed, in the first 5-10 seconds of the reaction was resulting in intense bubbling of the feed resulting in the feed getting out of the channels and depositing on the surface of the reactor. This deposition and the subsequent calculation of the coke yield, therefore, had no correlation with the diffusion path length the micro channels were providing. The experiments give an insight into the intensity of bubbling that can happen inside agglomerates, and that, micro channels as small as 120 microns in width are not enough for prevention of bubbling. It was found that despite leaving the channels, the feed did not leave the reactor and it deposited uniformly on both sides of the strip through which channels were machined, and the inner walls of the channels (Figure 4.6). The cracking reaction then proceeded on these surfaces for most of the 5 minutes duration of the reaction, as bubbling happens in the first 30 seconds of the reactions.

Ali et al. (2010) had run experiments on metal strips having thin films of vacuum residue, and coke yield was calculated by cracking of 20 and 80 μm thin films. Since the deposition on Reactor II seemed uniform and total (Figure 4.6), approximate film thickness was calculated by dividing the weight of the feed loaded by the surface area of Reactor II. The decrease in surface area on the top and bottom of the reactor due to channel pores was compensated by the deposition of feed on the inner walls of the channel. So the addition of the surface areas of the bottom and top sides of Reactor II gave the total surface area the feed was exposed to. The thickness of the film was calculated according to the following equation:

$$film_{thickness} * (2 * surface\ area\ of\ one\ side) * density_{feed} = \ mass_{feed}$$

The average film thickness was found to be 50 μm after six repetitions each for VTB and VTB 700+. The coke yield from this film thickness was compared with the coke yields obtained from 20 and 80 μm thin films experiments done by Ali et al. (2010). After normalizing the yields by the MCR of the feeds, the coke production factor for the 50 μm was found to be more than that from 20 μm films, and statistically not very significant when compared with 80 μm films (Figure 4.7). The findings were in line with the previous studies finding coke yield to increase with increase in film thickness in controlled liquid film geometry (Dutta et al., 2001; Gray et al., 2001; Radmanesh et al., 2008) as discussed in Section 2.4, although it must be kept in mind that calculations in this case were approximate due to the incidental deposition of feed on the surface of the reactor instead of remaining inside the channel pores.

Ways to prevent the feed from getting out of the channels is explored in Section 5.3.

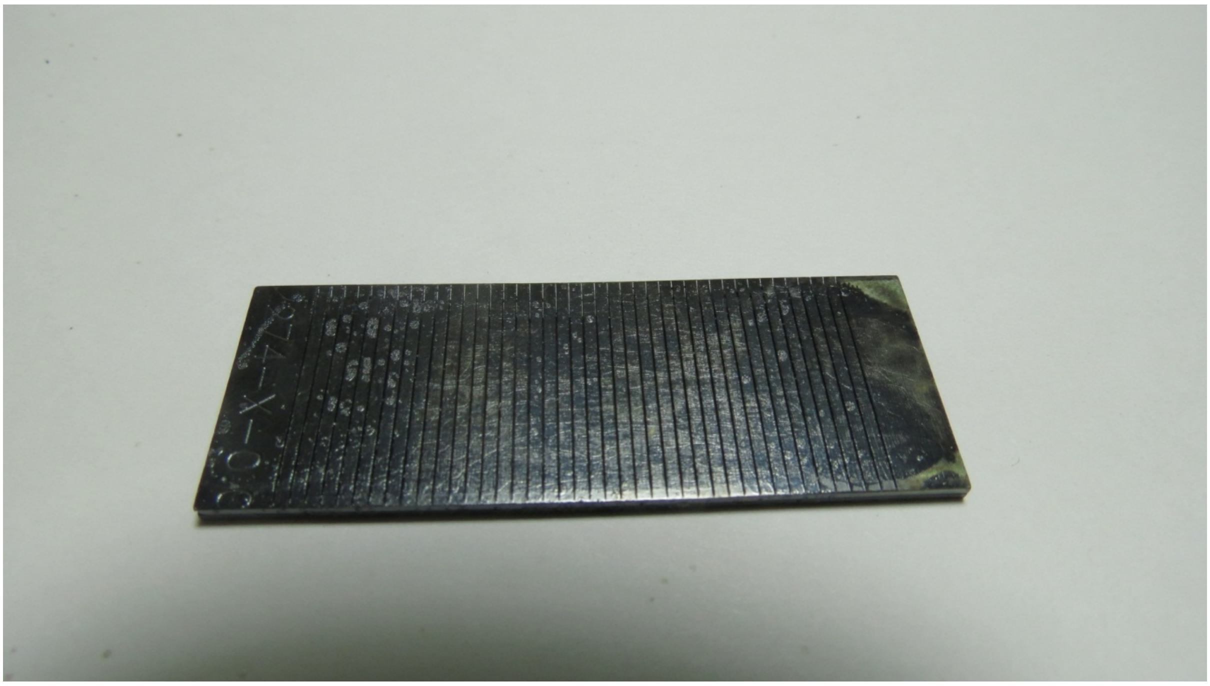

Figure 4.6 Reactor II after reaction. Deposits of coke can be observed throughout the surface.

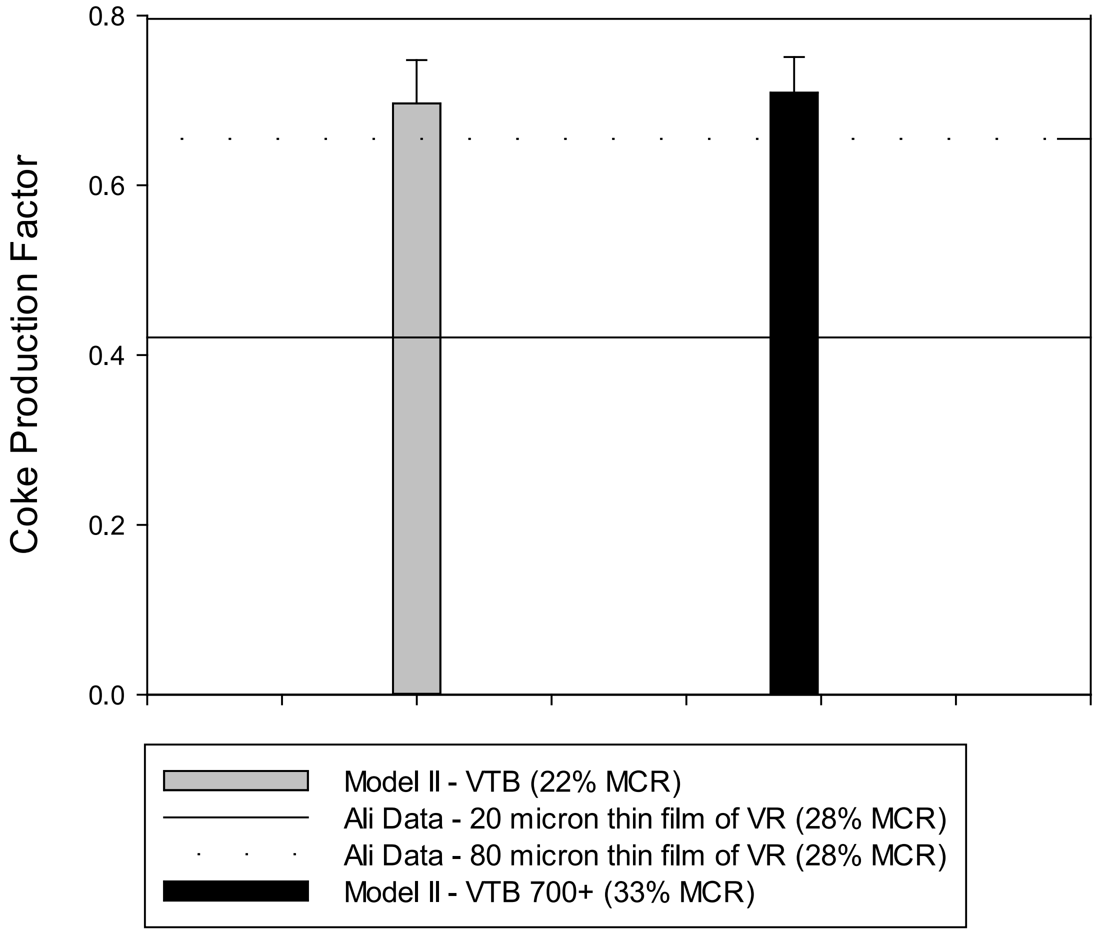

Figure 4.7 Comparison of coke yield from Reactor II with coke yields observed in 20 and 80 μm thin films in the work done by Ali et al. (2010) (number of runs =6). Error bars in y-axis represent the 95 % confidence interval from replicate experiments for finding coke production factors.

4.3 Cracking of Mixtures in Reactor III

VTB-coke mixture having 19.5% by wt of VTB was used for studying the formation of a skin of coke along the surface of the feed-coke mixture with the help of Reactor III. Well depths of 1.2 mm and 2 mm, i.e., Reactor Ia and Ib both were, in turn, used with Reactor II to form a 1.2 mm and a 2 mm capped Reactor III as discussed in Section 3.3.2.3. Six replicate experiments were done each with the 1.2 mm capped and the 2 mm capped Reactor III. The coke yields measured from cracking reactions in the 2 mm capped Reactor III were found to be the same as that of Reactor Ia (2mm), and also the coke yields from 1.2 mm capped Reactor III runs were found to be the same as that from 2 mm capped Reactor III after running statistical tests. However, comparing 1.2 mm capped Reactor III coke yields with those from Reactor Ia (1.2 mm open) indicated a statistical difference. Running an Anova test between the three sets then indicated a weak decreasing trend from Reactor Ia (1.2 mm open) to 1.2 mm capped Reactor III with the 2 mm capped Reactor III lying in between them (Figure 4.8).

The results are interesting in the sense that Reactor III was expected to promote differential rapid heating of the surface of the mixtures to encourage formation of a skin of coke, which would have given rise to increase in coke yields. However, the measured coke yields followed, if any, a weak reverse trend in the capped reactors. The reactor design was clearly unable to generate the intense heat at the top surface required to generate a layer of coke or skin on it, and might not be the best approach to check for the formation of a layer of coke on surface of mixtures.

There are a number of possibilities that could lead to these results. One should not forget that it is still a weak trend and the difference between consecutive values was not being detected by T tests. In the case where the Anova statistical test is giving a false positive, it would mean that there was no change in coke yields on going from uncapped to capped reactors. This would make absolute sense if the top heating source is just allowing for faster heating since we saw earlier that the rate of heating did not have an impact on the ultimate coke yields. The other option is that there is a weak trend among them. An explanation for this weak trend could be that since the vapors are escaping from the top, the heating from the top is resulting in rapid cracking at the top surface, and immediate escape of vapors from the reactor allowing formation of voids near the top surface. Void formation is, in turn, allowing easier escape of the subsequent cracked products resulting in lesser coke yield. Since all the capped reactors are exposed to the same surface area, the voids near the surface become a smaller fraction of the mixture as the well depth increases subsequently having a lesser effect in mixtures having larger thicknesses. This phenomenon could explain the decreasing trend of coke yields in capped reactors with the 1.2 mm capped Reactor III showing a greater decrease than the 2 mm capped Reactor III. Thus, all the open/uncapped reactors (Reactor 1) would show a higher coke yield because of absence of this effect. This occurrence would again be negligible in experiments of Ali et al. (2010) because of the higher thickness of the agglomerates. This rapid escape of vapors at the top resulting in void formation near the surface is different and unrelated from bubbling where redistribution of liquid phase within the mixture was a possibility. Bubbling, as discussed earlier, had no impact on ultimate coke yield. A third possibility would be an experimental error or procedure bias in getting the results. Liquid drainage in open/uncapped reactors affecting the coke yields is not a possibility since the coke insensitivity to well depth and bubbling goes against this hypothesis.

Looking at all the three possibilities, it is difficult to comment on which one is happening here and further investigation into it is a good option for the future scope of the project.

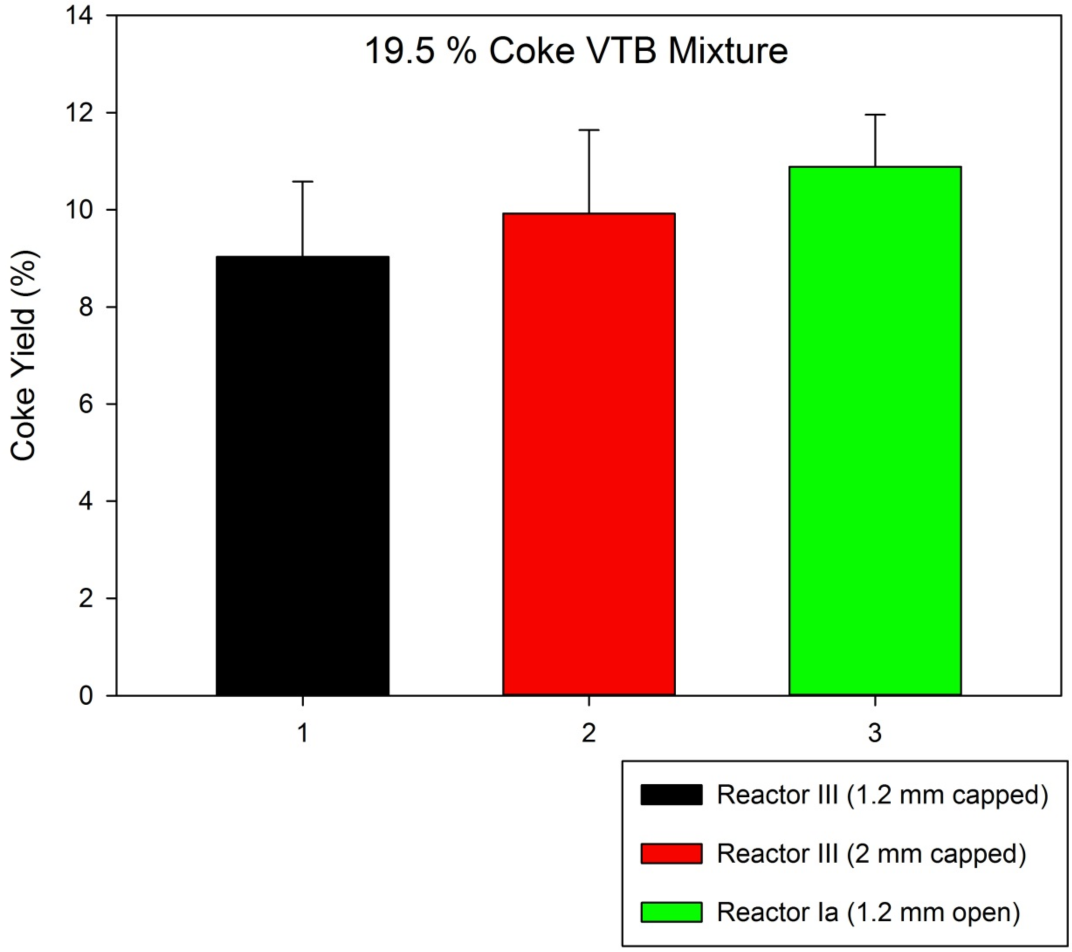

Figure 4.8 Comparison of coke yield from Reactor III with coke yields measured in Reactor Ia (number of runs =6). Error bars in y-axis represent the 95 % confidence interval from replicate experiments for finding coke yields.

5. Conclusions, Implications and Future Scope

5.1 Conclusions

The results obtained from this study illustrate the vital role of liquid saturation in agglomerates. Coke yield was found to increase with increase in liquid saturation in the range of 30 to 60%. The trend was observed in mixtures of all the three feeds tested, i.e., VTB, VTB 700+ and LC Finer Bottoms in this range of saturation. Since increase in liquid saturation is closely associated with increase in film thickness of liquid over coke particles, or increase in film thickness of liquid within agglomerates by forming bridges between particles, the findings were consistent with earlier studies showing the increase in coke yield with film thickness. At saturation levels higher than this, however, there is the possibility of liquid draining off from the agglomerate or getting ejected out of the agglomerate due to intense bubbling, both of which would lead to redistribution of liquid feed, consequently, a change in the liquid saturation of the agglomerates. Heating rate played a role in determining the intensity of cracking in the early stages of the reaction process, which could be observed in the form of greater bubbling. However, on running the reaction for a sufficiently long time, coke yields were insensitive to the variation in heating rates when tested in the range of 15°C to 110°C.

Coke yield was not affected by the change in the well depth of the reactor in the range of 0.6-2 mm, and consequently, it did not depend on the thickness of the mixture layer at that range. With the same ratio of liquid to coke particles in the different well depths, spreading of liquid over the coke particles is not affected by the thickness of mixtures in these ranges as seen by the insensitivity of coke yield towards this parameter. The liquid essentially cracks and travels to the surface through the empty pores since the mixture is not at full saturation and change in thickness does not affect this mechanism. This does not always have to hold true. In different thickness ranges, or by modifying other parameters such as the geometry of the reactors, there is a potential of coke yield depending on mixture thickness even with same liquid saturation due to the possibility of difference in heat and mass transfer within the mixtures.

Bubbling during reaction did not have an impact on coke yield at transitional liquid concentrations. The extent of bubbling being discussed here is only till the point where there was no escape of liquid from the reactor due to the intensity of bubbling. Bubbling was observed only in the initial 10-15 seconds of the timed 5 minute runs. The intensity increased with increase in heating rate but after running the reactions for a sufficiently long time, the coke yields were found to be independent of the presence or the intensity of bubbling. Bubbling increased with increase in liquid percentage in the mixture across all feeds and the intensity of bubbling reached its maximum when liquid feeds were used without any mixing with coke particles. The intensity was found to be so high at this point that it did not let the feeds stay stationary even in 120 micron thin channels.

At the range of thickness of mixtures used for the experiments, there was no evidence of formation of any skin on the outer surface of these mixtures as shown by the tests done in Reactor IIIa and IIIb. In the reactor corresponding to a well depth of 1.2 mm (Reactor IIIa), there was a decrease in coke yield at same liquid saturations as opposed to the potential increase as a result of formation of skin. No statistically significant change was observed in the coke yields when experiments were in Reactor IIIb (corresponding to a well depth of 2 mm).

5.2. Implication for Reactor Design and Operation

Agglomeration in fluid cokers is a significant concern for the industry as it tends to reduce the product yields and increase the rate of fouling in the reactor. Agglomerates give higher coke yields than thin films as demonstrated in the work by Ali et al. (2010). However, liquid saturation in agglomerates further impacts the coke yields as revealed by this study. Increase in liquid saturation within the agglomerates leads to higher coke yields, one of the key findings of this study. A high ratio of coke particles mixed with the amount of liquid feed entering the reactor is one criterion vital in ensuring minimal agglomerate formation and low liquid saturation within the agglomerates that are formed. Uniform distribution of feed among the coke particles is the other important factor as non-uniform distribution of liquid can lead to formation of agglomerates with high liquid saturations despite the presence of higher ratio of coke to feed in the overall reactor.

A more uniform liquid distribution, and giving a reduction of film thickness and agglomeration, can be achieved by effective modification of parameters such as feed atomization, orientation of feed nozzles, gas flow rate, and reactor length to diameter ratio (Gray, 2002). Design improvements to the feed nozzles, and use of multiple nozzles for spraying of liquid feed can improve the distribution of feed throughout the reactor (House et al., 2004, House et al., 2008, and McMillan et al., 2005). Reduction of feed droplet size with a feed atomizer can lead to formation of thinner films over the surface of coke particles (Tollefson et al., 1997). Increasing the amount of smaller coke particles in the reactor can also lead to improved reactor performance (Gray, 2002). Changing the type of feeds being used could also impact performance. VTB, in this study showed a higher sensitivity towards increase in wt fraction of liquid in the mixture. Throughput of heavier feeds could be increased without having a large increase in cpf. Figure 4.5 shows that there is a significant rate of increase in cpf of VTB-coke mixtures with increase in liquid fraction after 18 wt percent of VTB. So keeping liquid to solid ratio below this level for VTB could again possibly lead to improved performance.

A higher ratio of coke particles in the reactor and uniform liquid distribution can also reduce the amount of fouling taking place. As liquid particles and wet agglomerates impinge upon the walls of the reactors, liquid bridges are formed in case of a liquid film or a wet agglomerate being present on the reactor wall from before, forming a larger agglomerate. Higher ratios of coke and uniform liquid distribution can ensure reduced frequency of wet particles and agglomerates striking the walls allowing the liquid film or the agglomerate present on the surface to dry or drain off before another set of wet agglomerates strikes that region.

5.3 Differences between Industrial Reactor and Laboratory Setup

Experimental setup used in the study attempts to simulate the industrial reactor conditions in the fluid coking process closely as discussed in section 3.3. However, the difference in scale and design create a significant difference in product and coke yields. Coke production factors from the experimental setup varied from 0.3 to 0.7 while those from the industrial reactors are greater than 1.2. Absence of recycle in the experimental procedure is an important factor responsible for the disparity. With each recycle in the industrial reactor, percentage conversion of residue increases consequently resulting in greater coke yields. Effect of recycle on product and coke yields at lab scale was studied by Japanwala et al. (2002). Product yields increased by 12%, and coke plus gas yields increased by 5% after three stages of recycle during coking of Athabasca vacuum residue. Additionally, escape of vapors was immediate in the laboratory setup while some amount of vapors may undergo further cracking before their escape from the reactor in an industrial setting. Therefore, coke yields from the experimental setup would be expected to be less than that from the industrial process, which can be observed from the results of this study.

5.4 Future Scope

The results and findings of this study can form the basis for further work to better understand agglomeration inside fluid cokers in order to limit fouling and increase product yields in the process. Reactors made out of Alloy 52 played a major role in the rapid heat transfer provided to the mixtures and bitumen feeds in the induction furnace and the excellent control over their final reaction temperature. Reactor II gave insights into the intensity of bubbling and an approximate idea of the reaction in thin films of around 70 microns although it failed to achieve its initial goal of studying effect of diffusion path lengths on coke yields by coking reactions in micro channels. However, with design improvements to such reactors, it is possible to achieve its original purpose of providing control over diffusion path lengths in the reaction process. Reactor II can be modified by decreasing the thickness of the Reactor and decreasing the width of the micro channels. This would result in reduction in diffusion path length, and stronger capillary forces could prevent escape of liquid from the model during the reaction. Another approach towards better understanding of the industrial process could be to look at successfully generating a cpf similar to what is observed in the fluid coking process (about 1.2) in order to better pinpoint the factors giving a low cpf observed under lab conditions. For example, increasing the thickness of mixtures drastically, which could test the ability of coke particles in supplying heat within bigger agglomerates, could be one of the ways of doing this.

Attempts to generate a layer of coke on the surface or skin were unsuccessful in the present study. However, increasing the thickness of the mixtures by introducing spacers in between Reactor I and Reactor II can give insight into the unexpected trends of coke yield observed in the capped Reactor III. Significant increase in thickness can lead to changes in heat and mass transfer within mixtures.

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