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Development and Application of an Experimental Model for the Fluid Coking Process

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DEVELOPMENT AND APPLICATION OF AN EXPERIMENTAL MODEL FOR THE FLUID COKING^{TM} PROCESS

(Thesis format: Integrated Article)

by

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of
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Abstract

Liquid injection into a fluidized bed is used in industrial applications such as the Fluid Coking^{TM} process for heavy oil thermal cracking. Poor initial liquid-solid contact results in the formation of agglomerates that limit heat and mass transfer processes, reduce the yield of valuable compounds and create operating problems. The present study develops a new experimental model to simulate the complex phenomena that occur when heavy oil is injected in a Fluid Coker through two-phase nozzles. The model is applied in a pilot scale fluidized bed using scaled-down industrial spray nozzles. The experimental results indicate that agglomerate formation slows down liquid vaporization and that process conditions, such as bed hydrodynamics and temperature, have a significant impact on agglomerate properties. The experimental results also suggest how to modify spray nozzles to improve their performance in Fluid Cokers. Important information is provided for the development of the theoretical models that are needed to better understand the effect of agglomerating phenomena on bitumen upgrading.

Keywords

Fluid Coking^{TM}, Fluidized bed, Experimental modeling, Hydrodynamics, Agglomerates, Spray nozzle, Liquid vaporization

Co-Authorship Statement

Chapter 2

Article Title:
Experimental Modeling of Liquid Injection in a Fluidized Bed: Effect of Spray Nozzle Operating Conditions

Authors:
Carolina B. Morales M., Tarek J. Jamaleddine, Cedric Briens, Franco Berruti, Jennifer McMillan

Status:
Unpublished

Contributions:
Carolina B. Morales M. conducted all experimental work, analyzed the data and wrote the manuscript. Tarek J. Jamaleddine provided general guidance. The work was jointly supervised by Cedric Briens and Franco Berruti, who reviewed several drafts of this work. Jennifer McMillan provided useful advice throughout the project, ensured that the study was relevant to Fluid Coking$^{\text{TM}}$ and reviewed the final draft of the manuscript.

Chapter 3

Article Title:
Effect of Liquid Properties and Spray Nozzle Design on Agglomerate Properties in a Fluidized Bed

Authors:
Carolina B. Morales M., Tarek J. Jamaleddine, Cedric Briens, Franco Berruti, Jennifer McMillan

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Contributions:
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Chapter 4

Article Title:
Effect of Bed Hydrodynamics and Liquid Vaporization Rate on Agglomerate Properties in a Fluidized Bed

Authors:
Carolina B. Morales M., Tarek J. Jamaleddine, Cedric Briens, Franco Berruti, Jennifer McMillan

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Carolina B. Morales M. conducted all experimental work, analyzed the data and wrote the manuscript. Tarek J. Jamaleddine provided general guidance. The work was jointly supervised by Cedric Briens and Franco Berruti, who reviewed several drafts of this work. Jennifer McMillan provided useful advice throughout the project, ensured that the study was relevant to Fluid Coking^{TM} and reviewed the final draft of the manuscript.

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Nomenclature

GLR: Gas-to-liquid ratio (% wt/wt)
d_{aggl}: Agglomerate diameter (μm)
L/S: Liquid-to-solid ratio (g/g)
$\mathrm{d_{psm}}$: Sauter mean diameter (μm)
η: dynamic viscosity (mPa.s)
$\mathrm{V_g}$: fluidization velocity (m/s)
$\dot{\mathrm{m}}$: Liquid flowrate (g/s)
$\mathrm{m_c}$: mass of clean fines (g)
$\mathrm{m_p}$: mass of Plexiglas (g)
$\mathrm{m_{aggl,sample}}$: mass of agglomerates in sample (g)
$\mathrm{F_{vap}}$: Molar flow of vapors (mol/s)
$\mathrm{F_{N2,in}}$: Inlet flow of nitrogen (mol/s)
$\mathrm{T_{bed}}$: Temperature of fluidized bed (°C)
P: Pressure in the system (Pa)
V: volume of gases ($\mathrm{m^3}$)
n: total moles of vapors (mol)
ΔP: cyclone pressure drop (Pa)
R: Universal gas constant 8.314 Pa-$\mathrm{m^3}$/mol-K
M: Molecular weight of vapors (g/mol)
$\mathrm{T_{or}}$: Temperature at the orifice (°C)
x_{out}: fraction of vapors leaving the system
x_{in}: fraction of vapors evolving from the fluidized bed
$\mathrm{A_o}$: Initial Agglomerates
$\mathrm{A_f}$: Final Agglomerates
$\mathrm{m_s}$: flux of solid (kg/s)
$\mathrm{m_l}$: Liquid flowrate (kg/s)
$\mathrm{m_{vl}}$: vapors flowrate
$\mathrm{C_p}$: heat capacity (kJ/kg)
ΔH*: Effective heat of vaporization (kJ/kg)

Chapter 1

1 Introduction

Nowadays, the limited availability of light to mid-heavy oil reservoirs has resulted in the production of crude oil from non-conventional feedstocks such as heavy oil and bitumen[1]. Bitumen differs from conventional crude oil in its higher molecular weight and physical transport properties such as density and viscosity, thus making it unsuitable for pipeline transportation and for processing in conventional refineries. Therefore, it is necessary to upgrade this kind of heavy oil to produce distillates that can be transported and processed by conventional refineries[2].

Delayed coking and Fluid Coking^{TM} are the most commonly used commercial technologies for the production of distillates from bitumen through thermal cracking[3]. In the Fluid Coking^{TM} process, bitumen is sprayed into a fluidized bed of hot coke particles that serve as heating medium for the thermal cracking of hydrocarbons. The reaction takes place in liquid films deposited on the surface of the particles and the product hydrocarbon vapors rise to the top of the reactor counter-currently to the down-flowing coke particles. The high viscosity of bituminous feeds facilitates the formation of agglomerates with a thick liquid film that limits mass and heat diffusion from the particles, resulting in a decrease in liquid yield and increased production of undesired coke[4, 5].

This section includes an overview of the Fluid Coking^{TM} process and its associated agglomeration phenomena. Furthermore, the theory required for the development of a new experimental model applied to this process is presented here, to provide the background needed to fully understand its technical challenges and the experimental approach taken in this study.

1.1 The Fluid Coking^{TM} Process

A Fluid Coker consists of a circulating fluidized bed of coke particles acting as the heat carrier for thermal cracking of heavy hydrocarbon compounds, which typically include a heavy oil feedstock with 0° - 20° API[6]. When this process is used for bitumen upgrading, the feed oil is pre-heated to temperatures of 300 to 400 °C to make it flowable and injected with steam into the fluidized bed through several two-phase spray nozzles located at different axial and radial positions in the reactor section[7]. Figure 1-1 shows a diagram of the Fluid Coker where three main zones can be identified: a reactor section, where cracking and devolatilization of heavy hydrocarbon compounds take place, a scrubber section at the plenum of the reactor, and a stripper section of reduced diameter located at the bottom of the unit.

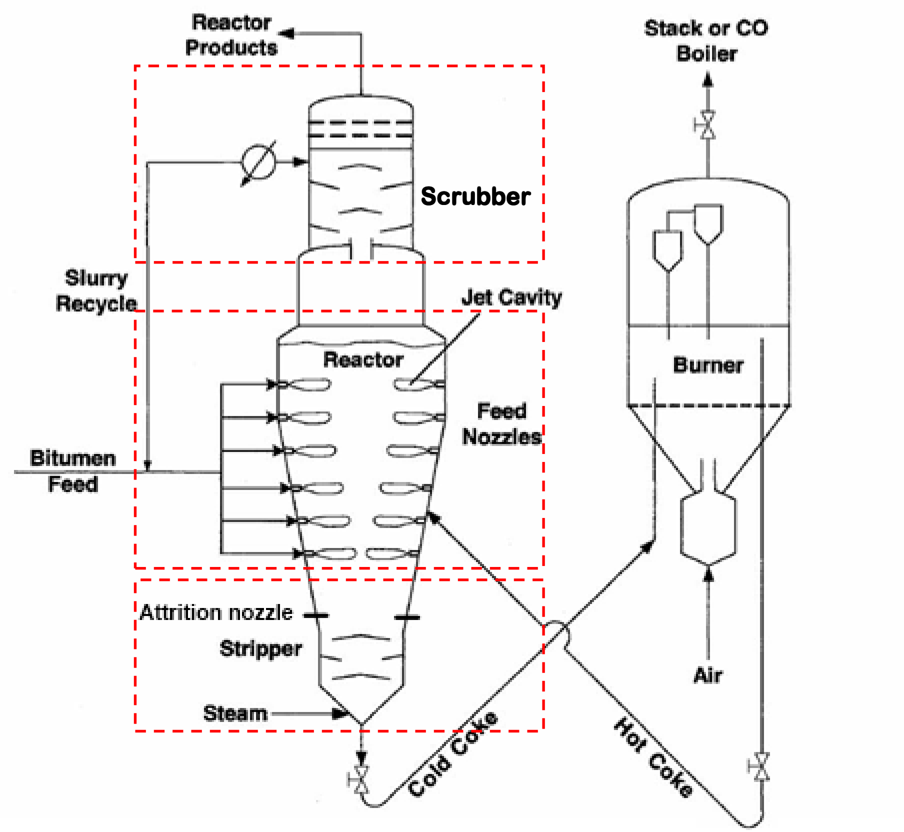

Figure 1-1: Schematic representation of Fluid Coking^{TM} Process[8]

Reaction takes place in a dense vapors-solids suspension at temperatures between 500 and 530 °C to produce permanent gases, oil vapors and coke. The permanent gases and vapor products are mixed with the steam used for fluidization and flow upward through a dilute phase freeboard, entraining some coke particles, which are recovered from the gas phase by cyclones and are returned to the bed through diplegs[8]. The product stream exiting the cyclones enters the scrubber section, where the heavier compounds are condensed and recycled to the dense fluidized bed, while the lighter gases and vapors continue on to the fractionation section (not shown in Figure 1-1) where they are condensed to undergo further processing[6].

Depending on the effectiveness of the initial liquid-solid contact in the dense suspension, agglomerates of bitumen and coke particles may form and will descend with the rest of the coke particles or, if excessively large, more rapidly segregate downward to the stripper section. The coke particles then grow larger as the coke byproduct of the hydrocarbon cracking reactions deposits on their surface. Supersonic steam attrition nozzles are used to maintain the particle size within the optimum range for good process operability. The stripper section uses steam to displace the hydrocarbon vapors from the voids in-between the downflowing particles, and the dry coke particles, free of hydrocarbons, are then sent to the burner drum, where they are re-heated from 480 to 700 °C and then recycled to the reactor[7].

1.2 Mechanism for Agglomerate Formation

Particle wetting and agglomerate formation have been previously described through two main mechanisms[9]:

1. In wetting by distribution, liquid droplets distribute on the surface of the particles and initial nuclei result from successful collision between wetted particles and wetted and dry particles, provided that certain energetic conditions are met. This type of mechanism predominates when the droplets mean size and the particle size are within the same range[10]. Therefore, this mechanism is promoted when the droplet size is minimized through an optimum nozzle design, a reduction in liquid viscosity or a high flowrate of atomization gas, for example
2. In wetting by immersion, initial nuclei are formed when a large droplet captures individual particles on its surface due to capillary forces[11].

In wetting by distribution, rather than wetting by immersion, the wettability of the system plays a significant role on agglomerate growth. Agglomerates are formed more easily if the surfaces of colliding particles are uniformly wet[12]. Otherwise, some of the liquid will have to be transferred first to the dry particle before a strong liquid bridge can be formed. It is, therefore, expected that liquids displaying low contact angles with the solid surfaces will facilitate this agglomeration mechanism.

Once nuclei are formed, agglomerates might growth from a balance between coalescence and breakage, due to the shear forces in the fluidized bed. The resulting agglomerate is a function of the strength of the initial aggregate formed which, in turn, depends on the amount and distribution of binding material holding the particles together. If these aggregates are strong enough, agglomerate growth will be dominated by coalescence of individual particles, whereas if the aggregates are weaker, they will exhibit significant fragmentation.[10]

In the Fluid Coking™ process, bitumen is injected together with steam through specially designed spray nozzles to form fine droplets that maximize liquid-solid contact and reduce agglomerate formation. The objective is to achieve a droplet size of 200 to 300 μm[7] and most of the agglomeration taking place is believed to occur via wetting by distribution at the end of the jet cavity created by the steam-bitumen sprays[11]. Given the high, average, concentration of dry particles in Fluid Cokers, it is expected that, in this particular case, agglomeration may also result from collisions between wet and dry particles, as the wet particles move from the tip of the jet cavity to the relatively dry bed. Moreover, due to the wide size distribution of coke particles in the Fluid Coker, some nuclei might also result from wetting by immersion of the particles. A more complex situation occurs when several small droplets hit the same area in quick succession: the droplets may then coalesce and capture several particles, combining wetting by distribution with wetting by immersion.

Gray et al.[12] proposed a mechanism for agglomerate formation in the Fluid Coking™ process composed by three main steps: in stage 1, liquid feed is introduced in the form of gas-atomized droplets in the fluidized bed and form a gas-liquid jet that entrains particles from the bed. Then, liquid droplets wet particles and agglomerates are formed in stage 2, which can break-up in stage 3, due to bed hydrodynamics and constant vapor evolution, resulting in smaller granules coated by a liquid film. However, the exact mechanism and kinetics for agglomerate formation in the Fluid Coking™ process is still unknown.

Darabi et al.[13] developed a mathematical model to describe the agglomerating outcome when bitumen droplets collide with coke particles and considered that agglomerates form when coke particles coated with a uniform bitumen film of a certain thickness collide, provided that specific conditions are met for successful collision to occur. Although their model incorporated the time-dependence of the physical properties of bitumen, breakage of agglomerates in stage 3 as proposed by Gray et al.[12] was not considered and a maximum agglomerate size was estimated without considering successful agglomeration between non-wetted particles.

Using X-ray movies of a gas-liquid spray interacting with a fluidized bed, Ariyapadi et al.[14] showed that wet agglomerates are formed near the tip of the spray jet cavity, where the liquid droplets meet with solid particles entrained through the jet and particles from the dense, emulsion phase of the fluidized bed. Ariyapadi et al.[15] developed a theoretical model to show that enhancing the mixing of entrained particles and liquid droplets within the jet cavity resulted in drier and weaker agglomerates; this was confirmed with experiments using a draft tube that enhanced radial mixing within the jet cavity.

Weber et al.[16] and Parveen et al.[17] studied the breakage of manufactured agglomerates in fluidized beds. They studied the impacts on agglomerate breakage of fluidization conditions, agglomerate size and shape, and liquid concentration in the agglomerates. They also investigated the effects of the properties of the constituent liquid and particles, such as viscosity, wettability, particle size, shape and density. Finally, Weber et al.[17] studied the stability of typical coke-bitumen agglomerates in a fluidized bed of coke particles at reacting conditions and showed there was extensive fragmentation of the agglomerates during fluidization; they also found that larger and wetter agglomerates were more stable.

Furthermore, the effect of process variables on the kinetics of agglomerate formation in the Fluid Coking$^{\text{TM}}$ process is still under study. Terrazas-Velarde et al.[19] demonstrated through a micro-scale modelling approach that the size distribution of agglomerates formed during fluidized bed spray drying is greatly affected by the binder properties, and that agglomerate growth is sensitive to process parameters such as binder viscosity and fluidization velocity. Therefore, in this study, attention is given to the effect of liquid properties, process parameters, and spray nozzle operating conditions on the three stages involved in agglomerate formation in Fluid Cokers.

1.3 Physical Properties of Bitumen

Previous studies have indicated that the main physical properties affecting liquid dispersion on particles and agglomerate formation are viscosity, surface tension and wettability, which is characterized with the contact angle[20]. Surface tension and viscosity are the main properties governing droplet size and spray quality in liquid atomization, while wetting of the particles and spreading on their surface is mainly a function of the contact angle[21]. It is then necessary to review these properties for bitumen at operating conditions and use these values as a reference for the development of a new experimental model that can mimic liquid dispersion on fluidized particles from gas atomized spray nozzles.

In the Fluid Coking^{TM} process, bitumen is injected at temperatures 300 – 400 °C through steam atomized nozzles. There is limited information on the accurate value for the viscosity of bitumen, due to the complexity associated with using current measurement techniques at elevated temperatures. However, it has been observed that bitumen viscosity is highly sensitive to temperature and reaction time. Aminu et al.[22] measured the viscosity of non – reacting Athabasca Vacuum Residue (AVR) bitumen provided by Syncrude Canada Ltd. at 180 °C and 270 °C, reporting values of 270 mPa.s and 150 mPa.s, respectively. The authors extrapolated these data and reported a value for bitumen viscosity at 400 °C in the range of 1 – 2 mPa.s. Other authors have reported bitumen viscosity at injection condition in the range of 3 – 4 mPa.s[11, 20] which could be associated to the viscosity at a lower temperature between 300 – 350 °C.

Once bitumen reaches 400 °C upon contact with the hot coke particles and the cracking reactions and devolatilization of the product start to occur, bitumen viscosity increases sharply with reaction time. Aminu et al.[22] also found that bitumen viscosity increased by four orders of magnitude, from its initial value of 1 – 2 mPa.s, to values in the order of 10^4 mPa.s. This rapid increase in bitumen viscosity at reacting conditions has been associated with the evaporation of lighter compounds in the feed and the cracking reactions resulting in a liquid film of much heavier and highly viscous hydrocarbon compounds.

On the other hand, the surface tension of bitumen is less sensitive to temperature at non – reacting conditions. However, some differences have been observed between dynamic and equilibrium surface tension. In this study, bitumen injection and rapid contact with the particles is believed to occur before bitumen reaches equilibrium conditions. Li et al.[21] studied the effect of temperature on the dynamic surface tension of nitrogen–saturated AVR bitumen from Syncrude Canada Ltd. The authors found that bitumen surface tension reaches equilibrium only after several hours and a linear relationship between the dynamic surface tension (γ_{Dyn}) and the temperature was given by:

$$\gamma_{Dyn} = 30.44 - 0.0376T \qquad (1.3)$$

Using Equation 1.3, the surface tension of bitumen can be then estimated in the range of 15.40 - 19.16 mN/m for temperatures of 300 to 400 °C. The authors also found that oxidation of bitumen with air or oxygen increases the surface tension of bitumen by 4%, resulting from changes in the distribution of polar groups upon oxidation. This effect of bitumen oxidation on the surface tension should be considered when running experiments in lab facilities where nitrogen–saturation conditions are not as well controlled as in the reactor unit.

Aminu et al.[22] also studied the surface tension of Athabasca bitumen at reacting conditions and, unlike viscosity dependence with reaction time, they found that the surface tension of bitumen was not affected by the extent of the reaction. Experiments were conducted at temperatures 400 – 530 °C and extrapolation of their values to lower temperatures were in good agreement with the results reported by Li et al.[21].

Wettability data for bitumen and coke are not available in the literature. To the best knowledge of the author, there is no direct measurement of the contact angle between bitumen and coke at temperatures of 300 – 400 °C. McDougall et al.[20] studied the effect of the contact angle on the agglomerating tendency of coke particles with a Sauter mean diameter of 135 μm, as the ones encountered in Fluid Coker. It was observed that for a liquid viscosity above 4 mPa.s, coke particles will always form agglomerates, regardless of the contact angle. However, as the liquid viscosity decreases below 4 mPa.s, as it is expected for bitumen at injection conditions, higher contact angles are needed for the formation of agglomerates, with a contact angle of 30° – 40° needed to form agglomerates of coke particles with a liquid viscosity close to 1 mPa.s.

When bitumen is injected in the Fluid Coker, the liquid jet is characterized by high velocities and bitumen droplets are believed to contact and wet entrained particles before they can reach higher temperatures. Then, a liquid viscosity at temperatures of 300 – 400 °C is considered in this study and, based on the agglomerating tendency of coke particles presented by McDougall et al.[20], a contact angle higher than 0° is expected for bitumen and coke at operating conditions.

1.4 Objectives of the Research

This thesis focuses on the development of a new experimental model than can be used to simulate in a lab facility the complex and interacting phenomena involved when bitumen is injected through steam atomized nozzles into a fluidized bed of hot coke particles. Efforts were concentrated on the development of a system that can be used at near ambient conditions and with scaled-down but realistic spray nozzles. This work has been divided in three sections:

Paper 1 (Chapter 2): A new model system comprised of a liquid solution and a solid is developed based on the physical properties of bitumen and coke at operating conditions, as reported in the literature. The model is tested in a large scale fluidized bed using a scaled down version of an industrial spray nozzle to study the effect of its operating conditions on the liquid distribution, agglomerate properties, and liquid vaporization.

Paper 2 (Chapter 3): Given the uncertainty in the physical properties of bitumen at injection conditions, this paper investigates the effects of liquid viscosity and wettability on agglomerate properties. The model is then extended to study the effect of spray nozzle design on agglomerate formation and liquid distribution.

Paper 3 (Chapter4): The proposed model is used to study the effect of bed hydrodynamics and bed temperature on the agglomerating phenomena observed in the Fluid Coking^{TM} process. The results obtained are expected to provide valuable information needed for a more systematic modeling of agglomerating mechanism, and its effect on the kinetics of thermal cracking of bitumen.

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Chapter 2

2 Experimental Modeling of Liquid Injection in a Fluidized Bed: Effect of Spray Nozzle Operating Conditions

2.1 Introduction

In the Fluid Coking^{TM} process, bitumen is sprayed through a series of steam atomized spray nozzles into a fluidized bed of recirculating hot coke particles. These particles act as the heating medium for thermal cracking of large hydrocarbon compounds at a temperature range between 500 – 530 ^{o}C, to produce a range of distillate products and coke as a by-product[1]. The by-product coke is deposited on the particles and, as a result, they grow in size. Once the coke particles reach the bottom of the reactor section, they enter the stripping section where they are exposed to high velocity steam jets which, through attrition, break large agglomerates and reduce the particle size, removing any hydrocarbon residue that might be trapped within the particles, before they are fed back to the burner bed. In the burner, the coke particles are reheated through partial combustion of coke and are fed back to the reactor at its top section. Figure 2-1 shows a simplified schematic representation of the process.

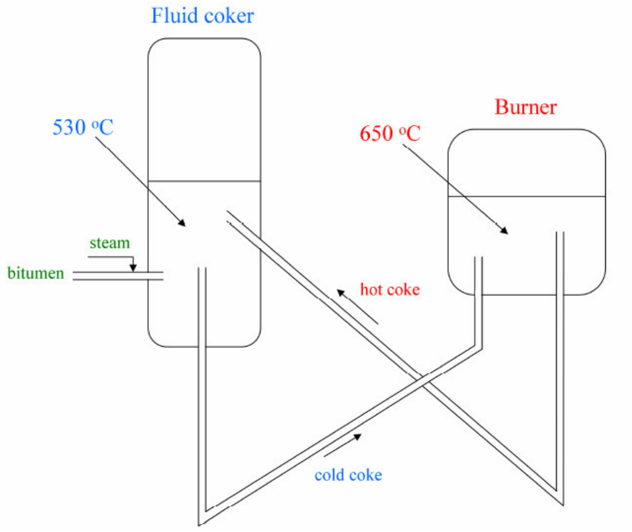

Figure 2-1: Schematic Representation of Fluid Coking^{TM} Process

Unlike the granulation process, where wet agglomeration of particles is desired, in the Fluid Coking^{TM} process, agglomerate formation is undesirable, since it results in heat and mass transfer limitations for the production of desired lighter compounds. As a result, lower liquid yields and higher coke yields are observed when agglomerates with a high liquid content are formed[2].

Several researchers have modeled the effect of agglomerates and agglomerate properties on heat and mass transfer limitations in the Fluid Coking^{TM} process. House et al.[2], showed that increasing the liquid to solid ratio (L/S) within the agglomerates reduces significantly the conversion of high boiling point compounds, which in turn results in higher coke yields. Similarly, Gray et al.[3] proposed a model to estimate the effect of mass transfer limitations on the liquid and coke yields, based on the relationship between the thickness of the liquid film and the diffusional resistance; this model predicted that thicker films of bitumen on particles would result in a higher coke yield.

Thermal cracking of large hydrocarbon compounds in the bituminous feed is followed by vaporization of the resulting lighter compounds from the liquid film. Li et al[4]. showed that the rate of vapors generation from the hydrocarbons injected in the Fluid Cokers has a significant impact on the hydrodynamics of the reactor, thus affecting the distribution of the injected liquid on the fluidized particles. However, their model did not consider agglomerate formation and breakup, which also affect the vaporization of the liquid.

The formation of agglomerates is a result of the imperfect initial liquid–solid contact, when bitumen is sprayed through steam atomized nozzles in the fluidized bed of coke particles. The study of these phenomena at a pilot plant scale level, using bitumen and steam at reacting conditions, would be impractical, expensive and relatively unsafe. As a result, different systems have been proposed to simulate, at near ambient conditions, the phenomena involved in the Fluid Coking^{TM} process when bitumen is sprayed with specially designed two phase nozzles. In this type of nozzle, atomization of the liquid and droplet size is a function of liquid flowrate and properties (viscosity, surface tension, and density), nozzle geometry, gas to liquid ratio (GLR), and fluid turbulence. However, the impact of these properties on nozzle performance will depend on the specific nozzle involved[5]. In a Fluid Coker, the bitumen will react, producing a mixture of vapors and permanent gases and a solid coke deposit on the bed particles.

Among these systems, water and silica sand have been used extensively to mimic liquid injection in the Fluid Coking^{TM} process using scaled down industrial spray nozzles, due to the similarity of the viscosity of water at ambient temperature and bitumen at injection temperature. However, the surface tension of water at ambient conditions (70 mN/m) is about three times higher than that of bitumen (15 – 20 mN/m), as presented in Chapter 1. Moreover, agglomerates formed in water – sand systems are easily broken upon drying, thus limiting this system only to the study of the initial dispersion of liquid within particles using indirect measurement techniques.

Similarly, coke particles along with an aqueous sucrose solution at ambient temperature have been used to characterize the initial liquid – solid contact of sprayed droplets on fluidized bed particles[2]. In this system, liquid viscosity is adjusted by selecting the proper sucrose concentration that will result in a similar value as that for bitumen at the injection temperature. Using this system at ambient conditions, it was possible to obtain stable agglomerates resulting from the binding action of the sugar upon drying that could be recovered after injection. These recovered agglomerates provided information on the size distribution of initial agglomerates and their liquid content. However, the high latent heat of vaporization of water was of concern for this model (Table 2-1). At ambient temperature, the evaporation of water is too slow to simulate the rapid evolution of vapors and gases in Fluid Coking^{TM}, which may have an impact on the formation and stability of agglomerates.

The sucrose solution was then used in a bed of coke particles at a much higher temperature in order to mimic the coke formation by caramelizing the sucrose content in the solution[6]. The fast evaporation of water also simulated the evolution of vapors and gases in Fluid Coking^{TM}, although the high latent heat of vaporization of water was still of concern as it was further increased due to the heat required to bring the liquid to the bed temperature, as shown in Table 2-1. Furthermore, there is an extra heat required for the caramelization reaction, which was unknown for these experiments. Unfortunately, once the sucrose was caramelized, much of the resulting caramel became insoluble and it was no longer possible to obtain information on the liquid content of the agglomerates. The objective of the present study is to develop a new experimental model to simulate, at near ambient conditions, the phenomena that occur when bitumen is injected in a Fluid Coker. Such a model could be used, for example, to determine the effect of spray nozzle operating conditions on agglomerate formation and liquid distribution within the agglomerates.

Table 2-1: Heat of vaporization for different systems

	Bitumen T_B: 530 °C	Water T_B: 21 °C	Water T_B: 250 °C
Energy required to heat the liquid from injection temperature to bed temperature (kJ/kg)	544	0	492
Latent Heat of Vaporization (kJ/kg)	430	2441	2441
Heat of Reaction (kJ/kg)	178	-	unknown
Total (kJ/kg)	1152	2441	2933

2.2 Experimental Set-up and Methodology

Experiments were performed in a large scale fluidized bed with a rectangular cross section of 1.2 m by 0.15 m and an expansion zone with a section of 1.2 m by 0.47 m at a height of 1.5 m from the ground (Figure 2-2). The unit was operated at 68°C with 150 kg of silica sand particles with a Sauter mean diameter of 210 μm, fluidized at a superficial gas velocity in the bottom section of 0.3 m/s resulting in an expanded bed height of 0.68 m. The liquid solution proposed for this new model is a mixture of acetone, pentane and Poly(methyl methacrylate) (PMMA) purchased from McMaster Carr, a polymer resin commonly known as Acrylic or Plexiglas^{TM}. This mixture of solvents was selected as it provided a lower latent heat of vaporization as it will be described in section 2.3. The liquid was injected horizontally in the dense fluidized bed, at 0.38 m above the distributor plate at 30 g/s for 42 s. This injection time was selected to reach steady-state evaporation and produce enough agglomerates to guarantee reproducible results. In order to achieve this liquid flowrate, the pressure on the liquid tank, shown as P2 on Figure 2-2, was adjusted by regulating the pressure of nitrogen from the main line. In this study, a scaled down version of an industrial nozzle used in the Fluid Coking^{TM} process, known as a TEB nozzle[7], was employed, having an internal diameter of 2.7 mm and using nitrogen at ambient temperature for atomization. In this case, the pressure on the atomization line, shown as P1 on Figure 2-2 was adjusted to obtain a specific atomization gas flowrate, expressed as GLR or Gas-to-Liquid Ratio (wt/wt). The unit was equipped with two cyclones in series, and the first cyclone recycled its collected fines to the bed through a dip-leg, while the fines collected by the secondary cyclone were recovered externally.

The bed was kept fluidized at minimum fluidization conditions for 10 min after each liquid injection in order to dry the bed while preserving the initial size distribution of the agglomerates. One sample port at the bottom of the unit allowed for the recovery of the bed material along with the agglomerates for further processing. Then, the collected bed mass was classified into three major groups:

- Macro-agglomerates: agglomerates recovered from the bed mass after injection having a diameter $600\ \mu m < d_{aggl} < 9500\ \mu m$
- Micro – agglomerates: agglomerates recovered from the bed mass after injection having a diameter $355\ \mu m < d_{aggl} < 600\ \mu m$
- Individual bed particles: all particles having diameter less than 355 μm

Macro-agglomerates were recovered by sieving the entire bed mass with the desired sieve size, since there were no initial bed particles with a diameter greater than 600 μm. The Plexiglas^{TM} concentration in these agglomerates was obtained by breaking up the agglomerates and using a Soxhlet extraction apparatus with acetone as a solvent to dissolve the Plexiglas^{TM} binder. Gravimetric analysis of the sample using a balance with an accuracy of 0.1 mg provided the mass of Plexiglas^{TM} that had been dissolved. In order to determine the dissolution time required to completely dissolve the Plexiglas^{TM} in the agglomerates, the samples were re-processed until no difference in the mass of the sample was observed. In addition, analysis of the solvent recovered with a Halogen moisture analyzer in subsequent washes verified that no dissolved Plexiglas™ was present. Once the amount of Plexiglas™ in the original solids sample was determined, the amount of liquid initially trapped in the agglomerates was calculated by mass balance, knowing the initial concentration of Plexiglas™ in the injected liquid.

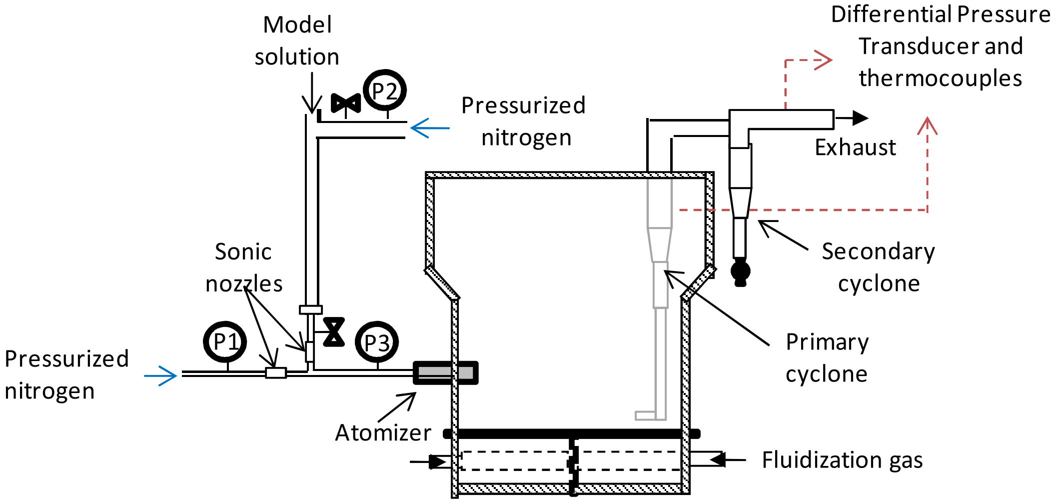

Figure 2-2: Schematic of the Large Scale Fluidized Bed

On the other hand, the size of micro-agglomerates falls within the size range of individual particles originally present in the silica used for the experiments. Then, fines trapped in these agglomerates were used as tracers to estimate the total mass of micro-agglomerates formed during the injection. In this case, once the bed mass had been sieved to recover macro-agglomerates, a representative sample from the bed mass below 600 µm was taken and processed with the same Soxhlet extraction apparatus described above. Particle size distribution of this sample was obtained using a laser diffraction method (HELOS of Sympatec), which provided information on the concentration of fines that were released upon dissolution of the liquid binder. The procedure involved three main steps:

1. Recovery of micro-agglomerates

Once the bed mass was sieved to recover macro-agglomerates (i.e. particles bigger than 600 µm), a representative sample was taken from the bed mass below 600 µm and sieved to be classified into three size cuts: 355 μm < dp < 425 μm, 425 μm dp < 500 μm and 500 μm dp < 600 μm. Each of these size cuts contained individual particles originally in the sand, along with micro-agglomerates formed during the experiments.

2. Determination of mass of Plexiglas^{TM} in the agglomerates

Samples were processed using a Soxhlet extraction apparatus with acetone as a solvent to dissolve the Plexiglas^{TM} binder. The washed particles were then dried. Gravimetric analysis of the sample using a balance with an accuracy of 0.1 mg provided the mass of dried washed sand particles (m_{sample}) and the mass of Plexiglas^{TM} that was been dissolved (m_p).

3. Determination of the mass of fine particles in the agglomerates

If the above mentioned size cuts are defined within a size limit from d_{pL} to d_{pH}, where each limit represent the smallest and biggest particle size for a given size cut, respectively, particles with a diameter below d_{pL} would have gone through the screen during the sieving process unless agglomerated. Then, if Figure 2-3 represents a particle size distribution (PSD) of the sample once step 2 has been completed, the concentration of fines (i.e. $d_p < d_{pL}$) in the sample can be determined from the PSD analysis.

Given the weight fraction of fines in the sample (x_f), and the weight fraction of fines originally in the bed mass, the mass of fines (m_c) was calculated as:

$$m_c = m_{sample} \times \frac{x_f}{x_{fbed}} \qquad (2.1)$$

where x_{fbed} is the weight fraction of fines in the bed. This assumes that there is no segregation in the way the different individual sizes of the bed particles are trapped within an agglomerate.

Then, knowing that the agglomerates are formed from sand and Plexiglas^{TM} only, the mass of agglomerates in the sample was calculated from the mass of Plexiglas^{TM} (m_p) obtained in step 2 and the mass of fines (m_c) from step 3:

$$m_{aggl,sample} = m_c + m_p \qquad (2.2)$$

This quantity represents the mass of micro-agglomerates for a given size cut in the sample. Then, the total mass of agglomerates was calculated as:

$$m_{aggl,total} = \frac{m_{aggl,sample}}{m_{sample}} \times \frac{m_{d_{pL}<dp<d_{pH}}}{m_{sample}} \times m_{<600\mu m} \qquad (2.3)$$

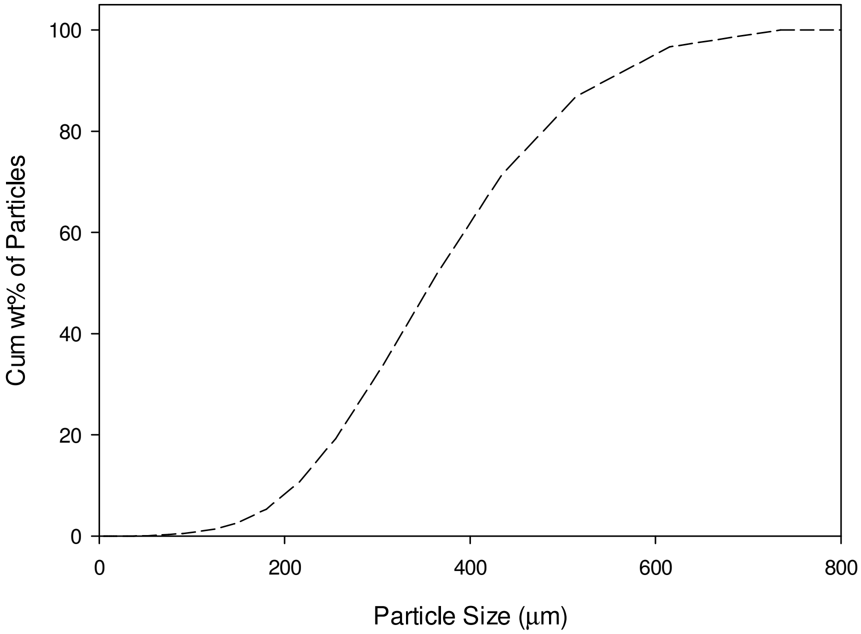

Figure 2-3: Particle Size Distribution of Washed Sand for a 355 μm - 425 μm Size Cut

Finally, differential pressure measurements between the freeboard and the outlet of the secondary cyclone were taken during the injection and the drying period. A simple flow model was developed as a first attempt to estimate the rate of injected liquid being vaporized in the bed. The calculation was based on three main assumptions:

1. Ideal gas behavior

This assumption allowed determination of the total number, ɳ, of gas moles in the column, including nitrogen and solvent vapors, considering the voids in between the particles. Then, a molar balance in the system is expressed as:

$$F_{vap} + F_{N_2,in} = \left(F_{vap} + F_{N_2}\right)_{out} + \frac{d\eta}{dt} \qquad (2.1)$$

Using the ideal gas law, the accumulation term was calculated as:

$$n = \frac{PV}{RT_{bed}} \Rightarrow \frac{d\eta}{dt} = \frac{V}{RT_{bed}}\frac{dP}{dt} \qquad (2.2)$$

The unit is discharging through the cyclones to the constant atmospheric pressure (P_{op}). Then, the variation of pressure with time can be expressed as:

$$P = P_{op} + \Delta P \qquad (2.5)$$

$$\frac{dP}{dt} = \frac{d\Delta P}{dt} \qquad (2.4)$$

Substituting this expression in Equation 2.1 results in:

$$\frac{d\eta}{dt} = \frac{V}{RT_{bed}}\frac{d\Delta P}{dt} \qquad (2.5)$$

Combining Equations (2.1) and (2.5) gives the final expression for the molar mass balance expressed as:

$$F_{vap} + F_{N_2,in} = \left(F_{vap} + F_{N_2}\right)_{out} + \frac{V}{RT_{bed}}\frac{d\Delta P}{dt} \qquad (2.6)$$

Note that vaporization of liquid in the bed will have an essentially instantaneous effect on the measured ΔP as the number of gas moles in the freeboard will increase instantaneously.

2. Orifice pressure drop

The standard correlations for cyclone pressure drop show that it is proportional to the gas density and the square of the gas flowrate[9]. This can be expressed as:

$$\Delta P = \frac{F^2 M T_{or}}{P} \qquad (2.7)$$

Then, if the above equation is used for the case of nitrogen as fluidization gas, this gives the pressure drop before the liquid is injected:

$$\Delta P_o = \frac{F_{N_2,in}^2 M T_{or}}{P} \qquad (2.8)$$

Temperature measurements across the cyclones indicated a nearly constant value during each experiment. Then, combining Equations (2.7) and (2.8), the following expression for the flowrate of vapors leaving the unit was obtained:

$$\frac{\Delta P}{\Delta P_o} = \left(\frac{F_{out} F}{F_{N_2,in}}\right)^2 \left(\frac{M}{M_{N_2}}\right) \qquad (2.9)$$

$$F_{out} = F_{N_2,in} \sqrt{\frac{\Delta P}{\Delta P_o} \frac{M_{N_2}}{M}} \qquad (2.10)$$

In the above expression, M is a function of the gas composition. If x_{out} represents the mole fraction of vapors across the cyclones, it can be expressed as:

$$M = x_{out} M_l + (1 - x_{out}) M_{N_2} \qquad (2.11)$$

$$M = M_{N_2} \left[1 + \left(\frac{M_l - M_{N_2}}{M_l}\right) x_{out}\right] \qquad (2.12)$$

3. Plug Flow in Freeboard

In order to determine the mole fraction of vapors in the cyclones (x_{out}), a plug flow model was assumed to find the oldest gas going through the cyclones, which corresponds to the fraction of vapor generated in the bed at a given earlier time called $t_{B.}$ Then,

$$x_{out}(t) = x_{in}\,(t_B) \quad (2.13)$$

From ideal plug flow, Δη moles leave the bed at a time interval Δt, and the total number of moles can be calculated as,

$$\eta = \int_{t_B}^{t} \Delta\eta\,(t_B)dt \quad (2.14)$$

Re-writing Equation (2.14) as a function of the molar flowrate evolving from the fluidized bed results in

$$\eta = \int_{t_B}^{t} F_{in}\,dt \quad (2.13)$$

where F_{in} represents the total molar flowrate, including nitrogen and solvent vapors. Since the flowrate of nitrogen used for fluidization is constant, Equation 2.13 can also be expressed as,

$$\eta = \int_{t_B}^{t} \left(F_{N_2,in} + F_{vap}\right) dt = (t - t_B)F_{N_2,in} + \int_{t_B}^{t} \left(F_{vap}\right) dt \quad (2.14)$$

Given that ideal gas law is assumed in this model, Equation 2.14 can also be written as:

$$\frac{PV}{RT_{bed}} = (t - t_B)F_{N_2,in} + \int_{t_B}^{t} \left(F_{vap}\right) dt \quad (2.15)$$

Then, the calculation procedure was as follows:

- Determine the value of t_B that satisfies Equation (2.15)
- Use this value of t_B to determine the fraction of vapors going through the cyclones at any given time (x_{out}), according to Equation (2.13)

- Combine Equations (2.6), (2.10), and (2.12) to calculate the flowrate of vapors evolving from the bed surface.

2.3 Results and Discussion

2.3.1 Development of the Model

In the present work, an experimental model applicable to the Fluid Coking^{TM} process was developed in order to overcome some of the limitations of previous models to study the effect of process parameters on agglomerate formation, liquid distribution and liquid vaporization. Then, three main phenomena involved in the Fluid Coking^{TM} process were considered:

- Initial liquid distribution upon spraying in the fluidized bed
- Agglomeration
- Liquid vaporization

In these processes, the physical properties of the liquid play an important factor. Therefore, a system whose properties were similar to bitumen and coke at operating conditions had to be identified. Furthermore, given the uncertainty on the properties of bitumen at injection conditions, it was also desirable to select a model that provided the flexibility needed to study the above mentioned phenomena under the range of values available in the literature for the industrial process of study.

In Fluid Coking^{TM}, bitumen acts as a liquid binder for the agglomeration of coke particles through a similar mechanism as the one observed in conventional granulation processes[10]. It has been reported in the literature that 10 to 20 wt% of the bitumen injected in a Fluid Coker produces a new layer of coke on the surface of the existing coke particles[11, 12]. Then, in the proposed model, the concentration of the Plexiglas^{TM} used as a dissolved binder was initially selected so that the amount of solid residue that remained on the particles upon vaporization of the liquid was similar to the coke yield observed in the industrial process (i.e. 10 – 20 wt%).

Plexiglas^{TM} was dissolved in a mixture of acetone and pentane, which was selected for two reasons:

1) It provides a solution with a low heat of vaporization as shown in Table 2-2, where the main difference with respect to the Fluid Coking^{TM} system is due to the higher energy required to increase the temperature from injection to reacting conditions. The impact of this higher energy could be studied, in the future, by chilling the model solution before it is injected.
2) The ratio between the solvents can be adjusted to obtain the desired contact angle (i.e. wettability) for the system. The Washburn technique described in Appendix A was used to study the effect of the acetone to pentane ratio on the wettability between the model solution and the silica sand particles. It can be observed from Figure 2-4 that the Plexiglas^{TM} concentration does not greatly affect the wettability of the system, unless the acetone-to-pentane ratio is significantly increased. Moreover, the contact angle can be varied over an even wider range by using different solids, as shown in Table 2-3. In the present study, a 10 wt% of Plexiglas^{TM} was selected with an acetone to pentane ratio of 8.0 wt/wt and Silica Sand particles, as it provided the best wettability for the system. The physical properties of this solution are presented in Table 2-4.

Table 2-2: Heat of vaporization for AVR from Syncrude Canada Ltd. (i.e. bitumen) and Model Solution (10 wt% Plexiglas^{TM} – 80 wt% Acetone – 10 wt% Pentane)

	Syncrude AVR	New Model
Energy required to heat the liquid from injection temperature to bed temperature (kJ/kg)	544	74
Latent Heat of Vaporization (kJ/kg)	430	451
Heat of Reaction (kJ/kg)	178	-
Total (kJ/kg)	1152	525

Table 2-3: Wettability of liquid solution (10 % Plexiglas^{TM}, Acetone-to-Pentane ratio: 8.0 wt/wt) determined by the Washburn technique

Solid	Contact Angle (°)
Silica Sand	32
Alumina	45
Coke	75

Table 2-4: Physical Properties of Model Solution

(10 % Plexiglas^{TM} – 80 % Acetone – 10 % Pentane)

	Syncrude AVR (400°C)	Model Solution (21°C)
Surface Tension (mPa.s)	21[4]	22.6
Initial viscosity (cP)	1 – 2[8]	2.2
Solid Particles (d_{psm})	Coke (135 µm)	Silica Sand (210 µm)
Contact Angle (°)	Not Available	32

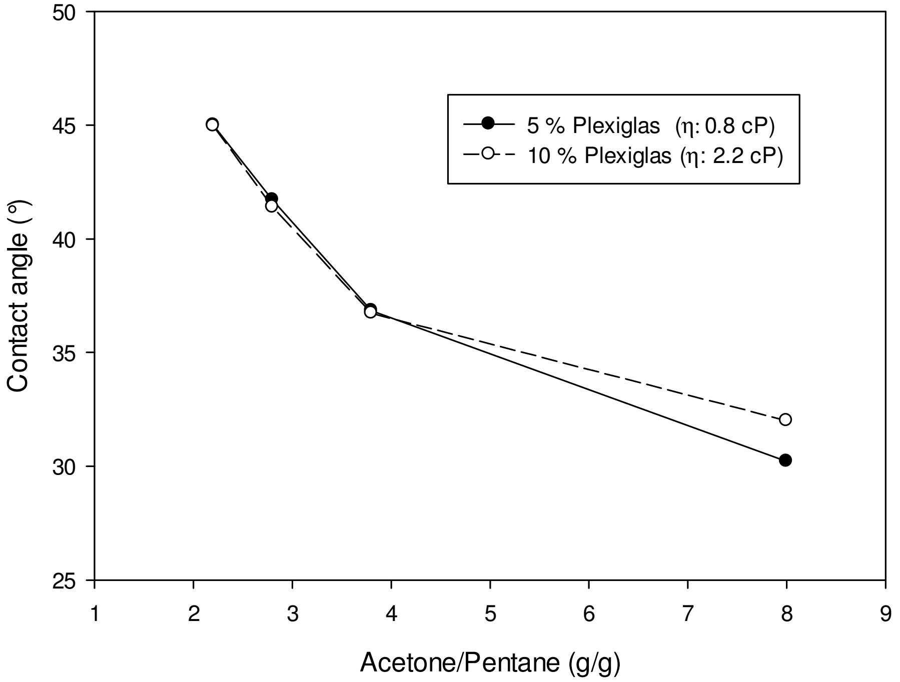

Figure 2-4: Effect of Acetone-to-Pentane ratio on the wettability of the system as determined from the Washburn technique.

2.3.2 Testing of the Model in a Large Scale Fluidized Bed

The initial experiments were focused on confirming the applicability of the proposed model for the study of agglomeration phenomena in the Fluid Coking^{TM} process. Experiments were performed under operating conditions similar to the conditions of previous studies using the sucrose solution model with caramelization[6]. The purpose of these experiments was to compare the impact of the atomization gas flowrate (expressed as GLR) in the spray nozzle on the total mass of agglomerates larger than 850 μm.

Figure 2-5 shows that the sucrose model gave a higher total mass of agglomerates than the proposed model for a given GLR. This could be a result of a higher liquid viscosity and higher wettability, along with smaller particles for the sucrose solution, as shown on Table 2-4, which in turn will lead to higher agglomerate population. The larger ratio of injected liquid mass to bed mass (L/S in Table 2-5) with the sucrose solution also promoted agglomerate formation.

Table 2-5: Operating Conditions for Validation Experiments

	Sucrose Solution[6]	**Plexiglas^{TM} Solution**
Spray Nozzle	TEB 2.7mm	TEB 2.7mm
Solids	Coke	Silica Sand
Sauter mean diameter	110 μm	210 μm
Liquid viscosity	3 cP	2.2 cP
GLR	3.6 %, 5.5 %	3.6 %, 5.5 %
Liquid Flowrate	30 g/s	30 g/s
Length of Injection	20 s	45 s
Total of liquid injected	600 g	1350 g
Mass of solids	22 kg	250 kg
liquid concentration in fluidized bed (L/S) (wt/wt)	0.0273	0.0054
$U - U_{mf}$	0.296	0.297

However, as previously indicated, the main objective was to determine the relative impact of the GLR on the agglomerates mass. Figure 2-5 shows that increasing the GLR from 3.6 to 5.5 wt% decreases the total mass of agglomerates by 13 wt% with the current model against 31 wt% with the sucrose model. Increasing the GLR in the spray nozzle will enhance the liquid-solid contact by decreasing the local L/S in the jet region[13]. Lower L/S values means that the liquid wets more particles and, consequently, fewer agglomerates are formed[2]. Therefore, these results may be explained by the liquid concentration in the bed, expressed as L/S in Table 2-4, which was three times higher for the sucrose model than for the current model, thus giving more opportunity for enhancement of liquid distribution through improvement of nozzle performance.

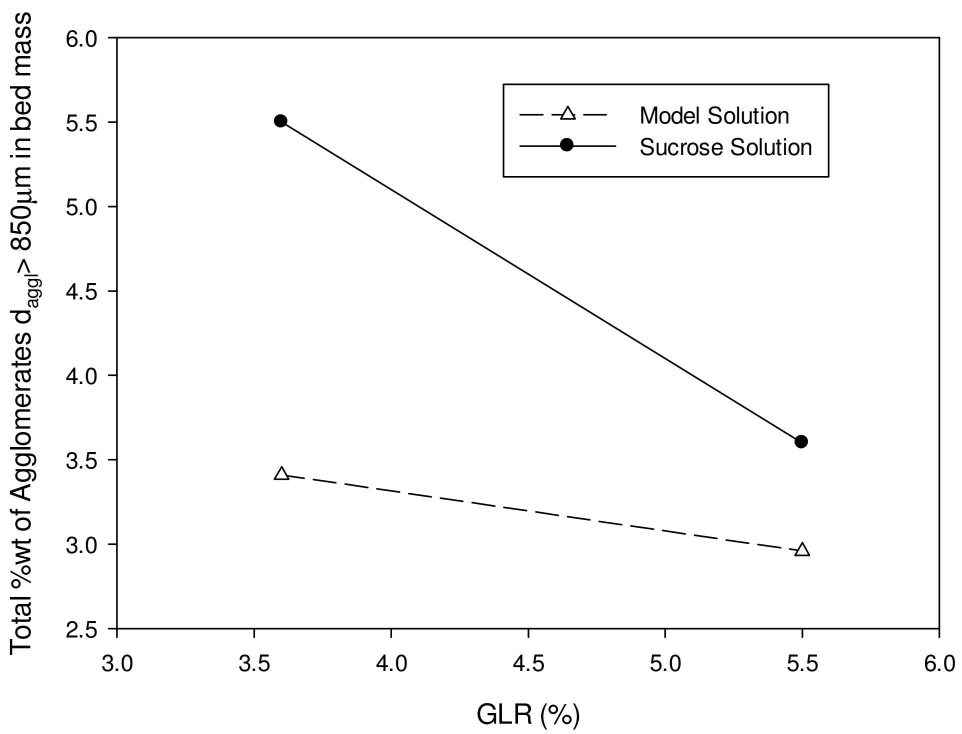

Figure 2-5: Comparison of the proposed model (10 wt% Plexiglas^{TM} – 80 wt% acetone – 10 wt% pentane) with the sucrose solution model, ṁ: 30 g/s, V_g: 0.30 m/s.

2.3.3 Effect of GLR on Agglomerate Properties

Further experiments were conducted with the proposed model solution in order to better understand the effect of the GLR on agglomerate properties. Figure 2-6 shows the repeatability of the methodology used for determination of agglomerates mass and size distribution. An average standard deviation of 0.057 wt% was observed for all the size cuts. Figure 2-7 shows the total mass of agglomerates formed for all the GLR values tested. The error bars show the variability in the results for two repeated runs. As expected, increasing the GLR decreases the total mass of agglomerates. These results are in agreement with findings from Portoghese et al.[13], where the effect of GLR on spray nozzle performance was assessed by means of triboelectric signals from the fluidized bed. In their work, experiments were conducted using the same spray nozzle geometry as the one used in the present study, and under similar operating conditions. The authors suggested that the improvement observed on nozzle performance when the GLR is increased is a result of smaller droplets at the tip of the nozzle, and a higher flux of solids entrained into the jet cavity. This in turn will result in better mixing in the jet region, evidenced in this work by lower liquid concentrations in agglomerates at higher Gas-to-Liquid ratios (GLR), as shown in Figure 2-8.

Furthermore, Figure 2-8 shows that small agglomerates exhibit a much lower liquid concentration as compared to bigger agglomerates. This can be explained by the proportion of the dry outer layer with respect to the inner liquid voids expected on the agglomerates, which seems to have a higher effect for small agglomerates.

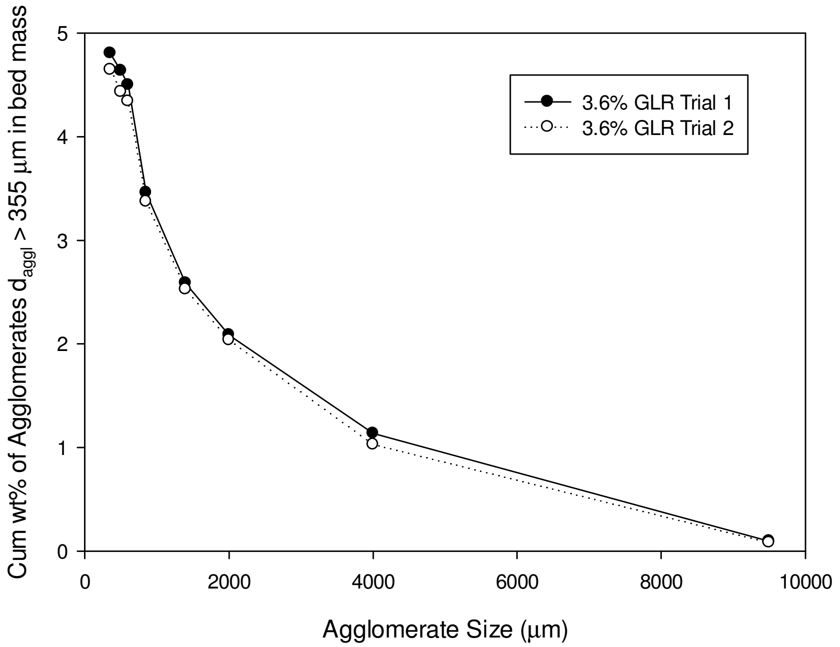

Figure 2-6: Repeatability of Methodology used for determination of agglomerate mass and size distribution, ṁ: 30 g/s, V_g: 0.30 m/s

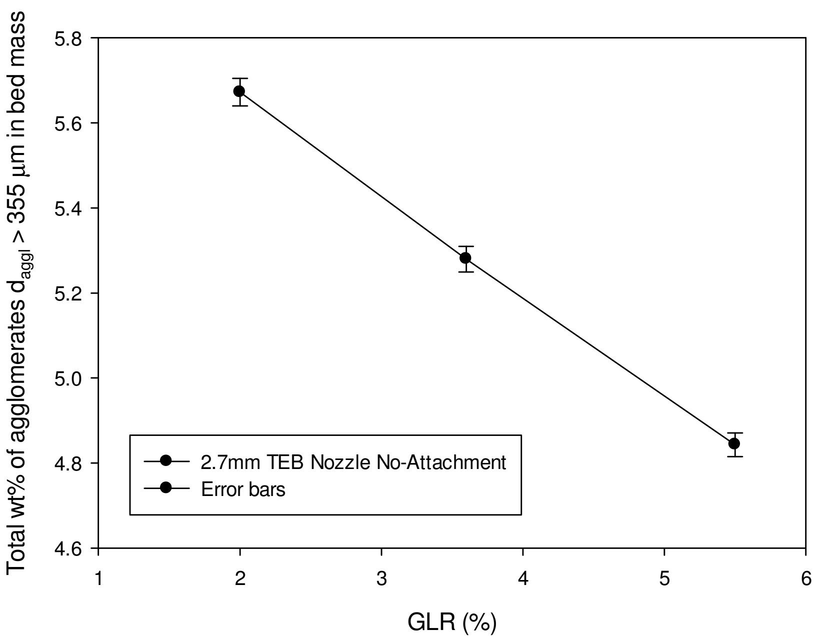

Figure 2-7: Effect of GLR on the total mass of agglomerates formed

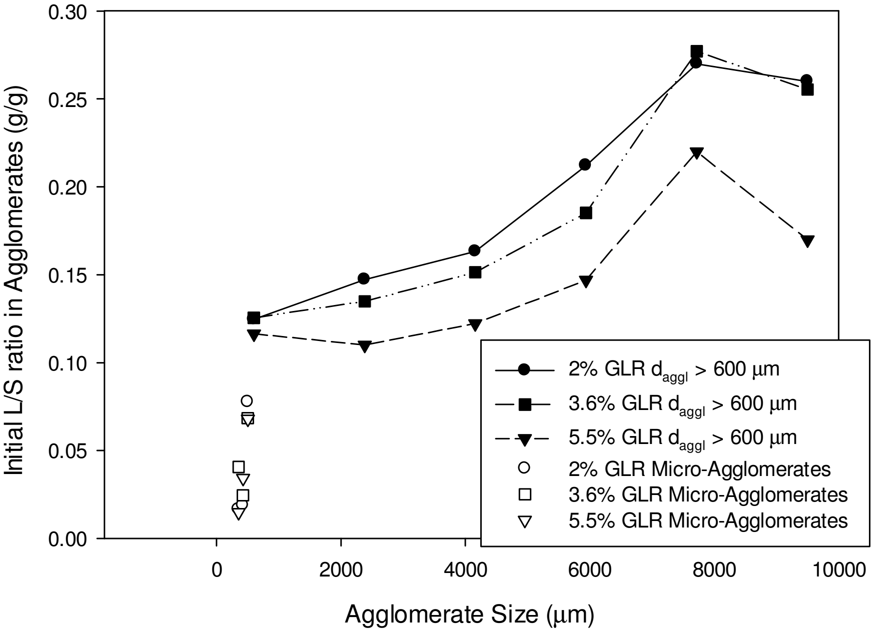

Figure 2-8: Effect of GLR on the initial liquid concentration in agglomerates, ṁ: 30 g/s, V_g: 0.30 m/s

2.3.4 Effect of Agglomerate Formation on Liquid Vaporization

Differential pressure measurements across the cyclones allowed for determination of two related parameters that characterize the vaporization rate of the liquid. These parameters are represented in Figure 2-9 and are defined as:

- Dissipation time (t_d): Time required to completely evaporate the liquid that is left in the fluidized bed after the end of the injection
- Residual Liquid (m_R): Mass of liquid that is left in the fluidized bed after the end of the injection.

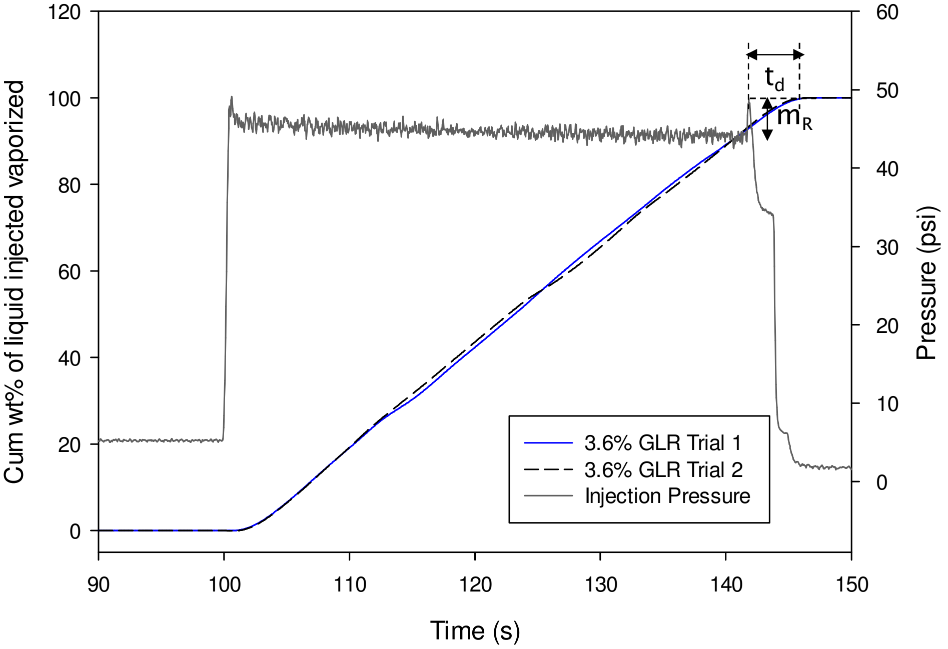

Figure 2-9: Dissipation time and residual liquid representation

In order to study the effect of agglomerate formation on the vaporization rate of the liquid, experiments were conducted using both pure acetone and the model solution. Figures 2-10 and 2-11 show a clear increase in both the dissipation time and residual liquid resulting from the presence of the liquid binder in the model solution. As the GLR in the spray nozzle is increased and fewer agglomerates are formed, a lower dissipation time and mass of residual liquid are observed. These findings are in agreement with the theory presented by other authors when looking into the effect of agglomerates and liquid distribution on heat and mass transfer processes taking place in Fluid Cokers[2, 3]. The results also suggest that using a fully vaporizable liquid, without a liquid binder such as Plexiglas^{TM}, underestimates the effect of agglomerates in the vaporization kinetics, thus confirming the importance of the use of the binder to better mimic the Fluid Coking^{TM} process.

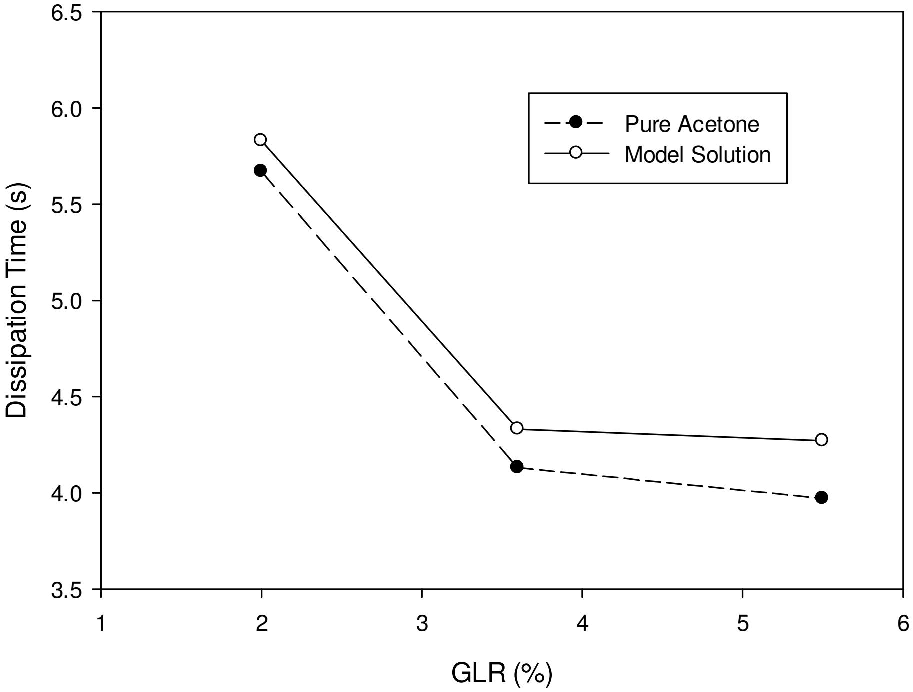

Figure 2-10: Effect of GLR on vaporization rate by means of dissipation time. Comparison between model solution (10 wt% Plexiglas^{TM} – 80 wt% acetone – 10 wt% pentane) and solvent only, $\dot{m}$: 30 g/s, V_g: 0.30 m/s.

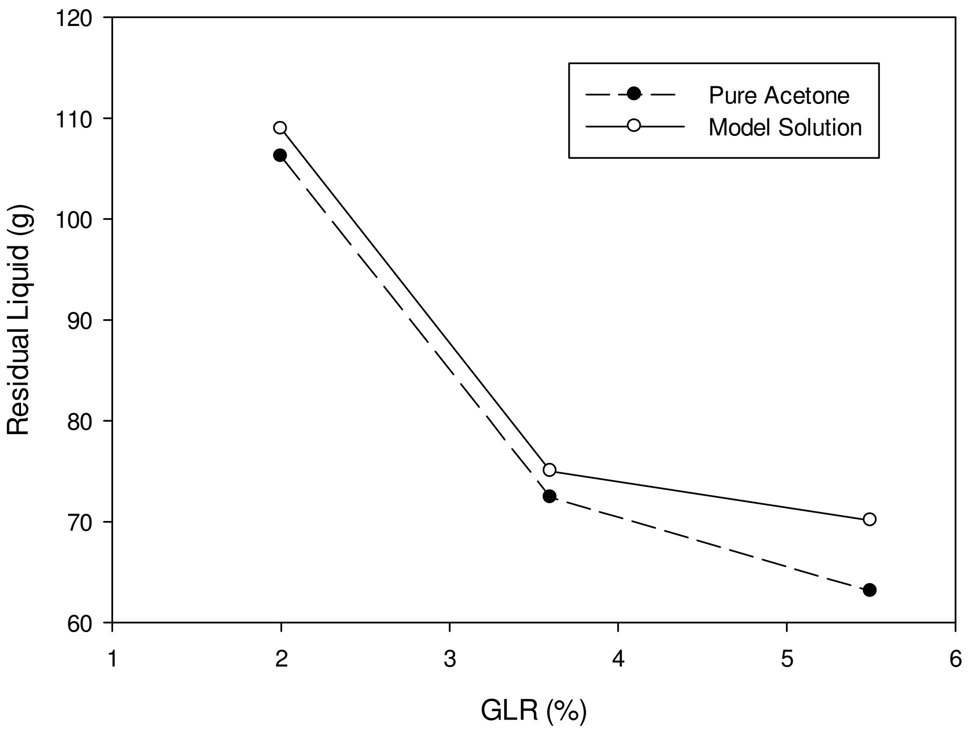

Figure 2-11: Effect of GLR and Agglomerate Formation on Vaporization rate by means of residual liquid. Comparison between model solution (10 wt% Plexiglas^{TM} – 80 wt% acetone – 10 wt% pentane) and solvent only, $\dot{m}$: 30 g/s, V_g: 0.30 m/s

2.4 Conclusion

The new proposed experimental model, consisting of the injection of a solution of Plexiglas^{TM} as a liquid binder and an acetone-to-pentane mixture as a solvent, in a fluidized bed of Silica Sand particles, is proven to be efficient and effective in studying the effect of spray nozzles performance on agglomerate formation. This new model resolves some constraints from previous models, such as a high latent heat of vaporization and high surface tension for the water-sand system, while providing additional useful information to support the theory behind the heat and mass transfer processes taking place in Fluid Cokers.

Experiments performed with the proposed model and a scaled down industrial nozzle showed that increasing the GLR will enhance the liquid distribution on fluidized particles, decreasing the formation of agglomerates and producing agglomerates with a lower liquid content to further minimize heat and mass transfer limitations. It was also possible to show, experimentally, that the formation of agglomerates with a higher liquid concentration decreases the vaporization rate of the liquid. In addition, the results illustrate the importance of a liquid binder in the model solution to better mimic the effect of agglomerate formation and its effect on the kinetics of bitumen upgrading.

2.5 References

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Chapter 3

3 Effect of Liquid Properties and Spray Nozzle Design on Agglomerate Formation and Liquid Vaporization

3.1 Introduction

Fluid Coking™ is one of the most commercial processes available for the production of distillates from bitumen by means of thermal cracking[1]. It comprises a recirculating fluidized bed of hot coke particles that act as the heating medium for thermal cracking of large hydrocarbon compounds at a temperature ranging from 500 to 550 °C, to produce a range of distillate products, with coke and non-condensable gases as by-products[2]. Once the coke particles reach the bottom of the reactor section, they are exposed to high velocity steam jets which, through attrition, break large agglomerates and reduce the particle size, before they are sent to the burner bed to be reheated through partial combustion of coke before being re-circulated back to the reactor at the top section. Figure 3-1 shows a simplified schematic representation of the process.

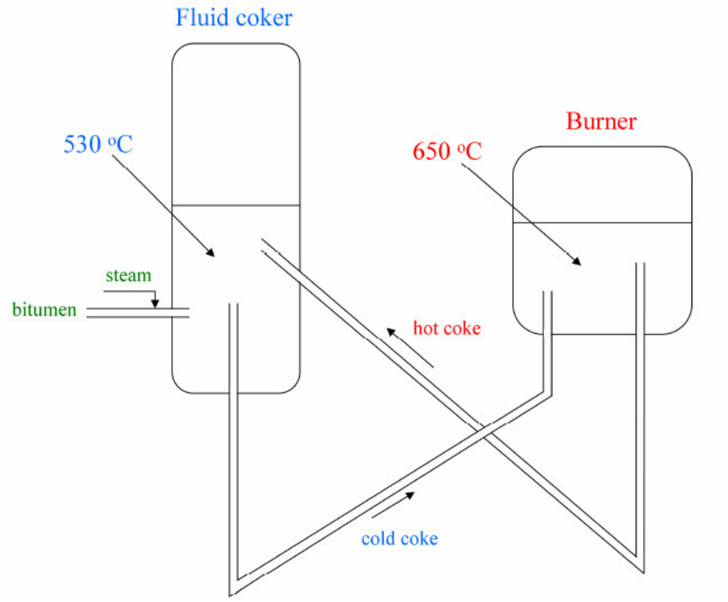

Figure 3-1: Schematic of Fluid Coking™ Process

In order to optimize liquid dispersion on the particles, bitumen is sprayed through a series of steam atomized nozzles oriented horizontally into the fluidized bed coker and positioned at different radial and axial positions of the bed[3]. The spray nozzle commonly used in today's Fluid Cokers is known as the TEB nozzle[4] (named after Terry Edward Base, who contributed the original design), which uses a convergent-divergent-convergent section to accelerate, decelerate and then accelerate again the gas-liquid flow and, thus, reducing the size of the resulting liquid droplets to desired values required for successful droplet–particle interactions in the fluidized bed (Figure 3-2). Bitumen and steam are pre-mixed before the nozzle entry and the two phase mixture travels through the horizontal piping of the nozzle. The rapid expansion of the steam at the nozzle exit and the high shear in the nozzle tip region cause the final inversion of the liquid from a continuous phase to a dispersed phase in the form of droplets[5].

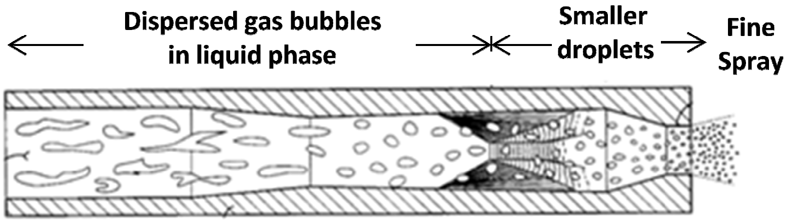

Figure 3-2: Cross-Sectional View of TEB Nozzle[4]

Ejim et al.[6] studied the effect of viscosity and surface tension on droplet diameter for a scaled down version of the conventional TEB nozzle used in industrial Fluid Cokers. A power law relationship exponent was observed in both cases, with the viscosity as the most predominant parameter. It was also suggested that using water at room temperature to simulate atomization of bitumen at operating conditions will result in droplets 30% bigger as compared to bitumen at 300 °C. This confirms the importance of proper selection of liquid properties for simulation of bitumen spraying phenomena using commercial available industrial nozzles, as discussed in Chapter 2.

Once the bitumen has been atomized in the form of fine liquid droplets, the steam-liquid jet forms a gas cavity with liquid droplets and entrained solid particles in the fluidized bed, known as the jet region. Previous studies have found that effective contact of liquid droplets with dry particles is achieved by a high solids entrainment into this high liquid flux region[7]. Poor initial contact of liquid droplets with the particles will result in the formation of agglomerates of high liquid content. These agglomerates can have detrimental impacts on the coking reaction by increasing the coke yield and decreasing the liquid yield[7,8].

Then, in order to improve feed atomization and minimize agglomerate formation, efforts have been focused on the optimization of the current TEB nozzle design. House et al.[9] used two different configurations of gas shrouds to improve mixing and entrain more solids into the jet cavity. It was found that such configurations improved feed distribution and reduced liquid concentration in agglomerates. Similarly, Saha et al.[10] found that these gas shrouds reduced the formation of large agglomerates responsible for heat and mass transfer limitations in the Fluid Coker.

House et al.[9] also found that placing a co-axial tube downstream of the spray nozzle improved liquid distribution. Their results were in agreement with experimental findings from McMillan et al.[11], who demonstrated the effectiveness of this co-axial tube to promote mixing of entrained solids with the liquid rich region. These results were later confirmed by Pougatch et al.[12], who employed a mathematical model to study the effect of this draft tube on jet-bed interactions. However, they found that, while the draft tube improved initial liquid–solid mixing in the jet region, the benefits were reduced at a distance of 10 cm from the nozzle exit, and completely disappeared at a distance of 30 cm from the nozzle exit.

Furthermore, Pougatch et al.[13] studied the effect of different conical attachments to the original TEB nozzle on jet expansion and jet–bed interactions. They found that the addition of these attachments can have beneficial or negative effects on the jet–bed interface, depending on the conical angle of the attachment used, where the performance of the original TEB nozzle was found to be somewhere in between the different configurations studied.

On the other hand, as introduced in Chapter 2, agglomerate formation does not only depend on proper liquid distribution, but also on the properties of the liquid and its affinity with the solid particles. Several investigations have found that the agglomeration mechanism of wet particles is a function of the physical properties of the liquid such as viscosity, surface tension, and wettability or contact angle[14]. Models for wet agglomeration suggest that stronger agglomerates are formed when the viscosity and surface tension of the liquid increase and the contact angle decreases[15,16]. These findings were confirmed by Weber et al.[17] for conditions relevant to the Fluid Coking™ process. It was observed that, while more viscous liquids produce stronger agglomerates, fragmentation of those agglomerates was not significant when the contact angle of the liquid-solid system was increased. However, McDougall et al.[14] found that the agglomeration tendency of coke particles, as the ones used in the Fluid Coking™ process, is affected by the wettability of the system. It was observed that the minimum contact angle required for successful agglomeration of coke particles was higher than 40° for a liquid binder with a viscosity below 2 mPa.s, while the contact angle required for liquid viscosities in the range of 3 – 4 mPa.s was below 20°.

As it was presented in Chapter 1, availability of accurate values for the physical properties of bitumen at injection conditions is limited due to the complexity of using existing measurement techniques at injection and reaction conditions. Surface tension values of bitumen have been reported in the range of 15 – 21 mN/m[18,19], for temperatures between 300 – 400 °C. On the other hand, bitumen viscosity under conditions when the reaction is still significant is more sensitive to increasing temperatures and has been reported between 1 – 2 mPa.s and 3 – 4 mPa.s for temperatures of 300 and 400 °C, respectively.

This chapter is divided into two main sections. First, the effect of liquid properties on agglomerate formation and liquid distribution is studied. Then, two different configurations of the original TEB nozzle are used to study the effect of spray nozzle geometry on agglomerate properties and liquid vaporization.

3.2 Experimental Set-up and Methodology

Experiments were performed in a large scale fluidized bed with a rectangular cross section of 1.2 m by 0.15 m and an expansion zone with a section of 1.2 m by 0.47 m at a height of 1.5 m from the ground (Figure 3-3). The unit was operated at 68°C with 150 kg of silica sand particles with a Sauter mean diameter of 210 μm, fluidized at a superficial gas velocity in the bottom section of 0.3 m/s, resulting in an expanded bed height of

0.68 m. The unit was equipped with two cyclones in series, where the first cyclone recycled its collected fines to the bed through a dip-leg, while the fines collected by the secondary cyclone were recovered externally.

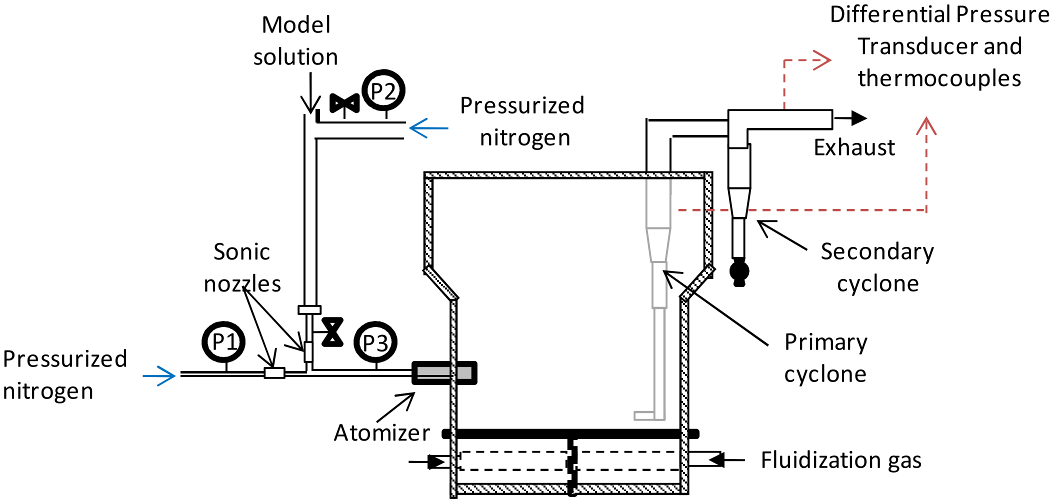

Figure 3-3: Schematic of the Large Scale Fluidized Bed

In order to study the effect of liquid properties on agglomerate formation and liquid distribution, a modified form of the liquid solution presented in Chapter 2 was used, and its physical properties are compared with those of the previous solution in Table 3-1. The solution at ambient temperature was injected horizontally in the dense fluidized bed, 0.38 m above the distributor plate at 30 g/s for 42 s. This injection time was selected to reach steady-state evaporation and produce enough agglomerates to guarantee reproducible results. In order to achieve this liquid flowrate, the pressure on the liquid tank, shown as P2 on Figure 3-3, was adjusted by regulating the pressure of nitrogen from the main line. In this study, a scaled down version of the TEB nozzle used in the Fluid Coking^{TM} process was employed, with an internal diameter of 2.7 mm using nitrogen at ambient temperature for atomization of the liquid phase. In this case, the pressure on the atomization line, shown as P1 on Figure 3-3 was adjusted to obtain a Gas-to-Liquid ratio (GLR) of 2 % (wt/wt). This value was selected as it most closely represents the values used in the industrial process.

Experiments were conducted with the conventional TEB nozzle described in section 3.1 and two modified TEB nozzles, with the purpose of studying the effect of nozzle design on liquid distribution and liquid vaporization. The first of these two modified nozzles consisted of a specially designed attachment at the tip of the TEB nozzle, known as the "Clover Leaf" attachment[20] and shown in Figure 3-4. The second nozzle used was first introduced by House et al.[9] and consisted of three sonic gas jets with an inner diameter of 0.4 mm surrounding the TEB Nozzle at a distance of 25.4 mm from its axis. This configuration is referred to in this study as the "Satellite Nozzle" and it is shown in Figure 3-5. The global GLR was kept constant at 2 % (wt/wt) and it was distributed to direct 54 wt% of the atomization gas going through the main TEB nozzle and 15.33 wt% of the gas through each of the peripheral gas jets.

Table 3-1: Physical Properties of Model Solution

	Syncrude AVR (300 – 400 °C)	Model Solution 1 used in previous studies (Chapter 2) (21 °C)	Model Solution 2 introduced for this study (21 °C)
Plexiglas™/Acetone/Pentane		10 %/ 80 %/ 10 %	5 %/ 60 %/ 35 %
Surface Tension (mPa.s)	15 - 21[4]	22.6	19.47
Initial viscosity (cP)	1 – 2[7]	2.2	0.8
Solid Particles (d_{psm})	Coke (135 µm)	Silica Sand (210 µm)	Silica Sand (210 µm)
Contact Angle (°)	Not available	32	45

Figure 3-4: 2.7 mm TEB Nozzle with Clover Leaf Attachment[20]

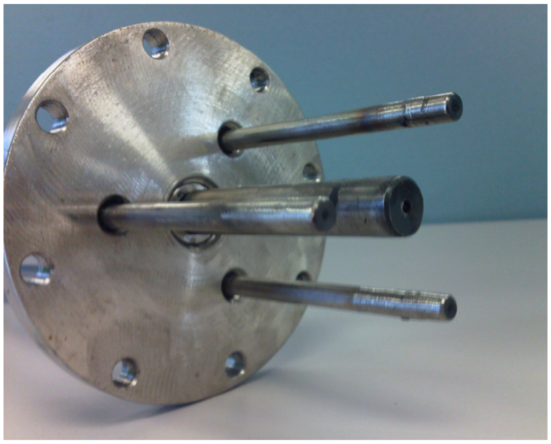

Figure 3-5: 2.7 mm TEB Nozzle with three 0.40 mm Satellite Jets[10]

The bed was kept fluidized at minimum fluidization conditions for 10 min after liquid injection, in order to dry the bed while preserving the initial size distribution of the agglomerates. One sample port at the bottom of the unit allowed for recovery of the bed mass along with the agglomerates for further processing. The bed mass was classified into three major groups:

- Macro-agglomerates: agglomerates recovered from the bed mass after injection having a diameter $600\ \mu m < d_{aggl} < 9500\ \mu m$
- Micro – agglomerates: agglomerates recovered from the bed mass after injection having a diameter $355\ \mu m < d_{aggl} < 600\ \mu m$
- Individual bed particles: particles having a diameter less than 355 μm

Macro-agglomerates were recovered by sieving the entire bed mass with the desired sieve size, since there were no initial bed particles with a diameter greater than 600 μm. The Plexiglas^{TM} concentration in these agglomerates was obtained by breaking up the agglomerates and using a Soxhlet extraction apparatus with acetone as a solvent to dissolve the Plexiglas^{TM} binder. Gravimetric analysis of the sample using a balance with an accuracy of 0.1 mg provided the mass of Plexiglas^{TM} that had been dissolved. In order to determine the dissolution time required to completely dissolve the Plexiglas^{TM} in the agglomerates, the samples were re-processed until no difference in the mass of the sample was observed. In addition, analysis with a Halogen moisture analyzer of the solvent recovered in subsequent washes verified that no dissolved Plexiglas^{TM} was present. Once the amount of Plexiglas^{TM} in the original sample had been determined, the mass of liquid initially trapped in the agglomerates was calculated by mass balance, knowing the initial concentration of Plexiglas^{TM} in the injected liquid.

On the other hand, the size of micro-agglomerates falls within the size range of individual particles originally in the silica used for these experiments. Then, fines trapped in these agglomerates were used as tracers to estimate the total mass of micro-agglomerates formed during the injection. In this case, once the bed mass had been sieved to recover macro-agglomerates, a representative sample from the bed mass below 600 μm was taken and processed with the same Soxhlet extraction apparatus described above. Particle size distribution of this sample was obtained using a laser diffraction method (HELOS of Sympatec), which provided information on the concentration of fines that were released upon dissolution of the liquid binder. This, along with the mass of Plexiglas^{TM}, allowed estimation of the total mass of micro-agglomerates in the sample. Detail procedure for this calculation is presented in Chapter 2.

Finally, differential pressure measurements between the freeboard and the exit of the secondary cyclone were taken during the injection and drying period. A flow model was then used to estimate the rate of injected liquid being vaporized in the bed. Major assumptions of this model included:

- Ideal gas behavior. This allowed determination of the total number of moles in the freeboard, including nitrogen and solvent vapors
- Cyclone pressure drop is proportional to the square of the gas molar flowrate and gas molecular weight
- Plug flow of gas in freeboard

Detailed equations used in this model can be found in Chapter 2.

3.3 Results and Discussion

3.3.1 Effect of Liquid Properties on Agglomerate Formation and Liquid Distribution

Physical properties of the liquid solution used in this study were modified by decreasing the Plexiglas^{TM} concentration and Acetone-to-Pentane ratio with respect to those used for the work presented in Chapter 2. This resulted in a decrease in liquid viscosity and wettability of the system (Table 3-1). The agglomeration mechanism for the Fluid Coking^{TM} process proposed by Gray et al.[21] and discussed in Chapter 1, is considered in this work to be divided in three stages as presented in Figure 3-6:

- Stage 1: Initial distribution of liquid sprayed in the form of fine droplets among entrained particles in the jet cavity, which include the impact of liquid droplets on the solids at the tip of the jet cavity

- Stage 2: Wetting and spreading of the liquid on the surface of the particles and formation of agglomerates in the jet

- Stage 3: Break-up of agglomerates due to shear forces and destabilization of the wet agglomerates, as a result of constant cracking and devolatilization of the product

Each of these stages is believed to affect the properties of the agglomerates formed as follows:

- In Stage 1, improvement of the initial liquid distribution will result in smaller liquid droplets contacting more entrained particles in the jet cavity, resulting in fewer agglomerates formed with lower liquid concentrations[7]. This can be achieved, for example, by lowering the viscosity of the liquid, resulting in smaller droplets formed in the spray, or by using a more effective spray nozzle.
- In Stage 2, the formation of a liquid bridge between colliding particles is favored if both particles are wet. Then, when the wetting mechanism is improved in stage 2, the liquid covers a higher surface area of the particle more easily and, as a result, lower amounts of liquid are required for successful agglomeration,

resulting in drier agglomerates that can survive the shear forces in the bed, thus increasing the total mass of agglomerates formed. Increasing the wettability by decreasing the contact angle should, therefore, result in agglomerates with a lower binder concentration and a larger total mass of agglomerates.

- In Stage 3, if break-up of the particles is enhanced, only the stronger agglomerates with a high liquid concentration will survive and, as a result, a higher mass of smaller agglomerates with a higher binder concentration is expected. However, the final result can vary depending on the break-up mechanism dominating, which is a very complex process as presented by Weber et al.[17]. This can be achieved, for example, by increasing the superficial gas velocity and hence the shear forces acting on the agglomerates when they encounter gas bubbles.

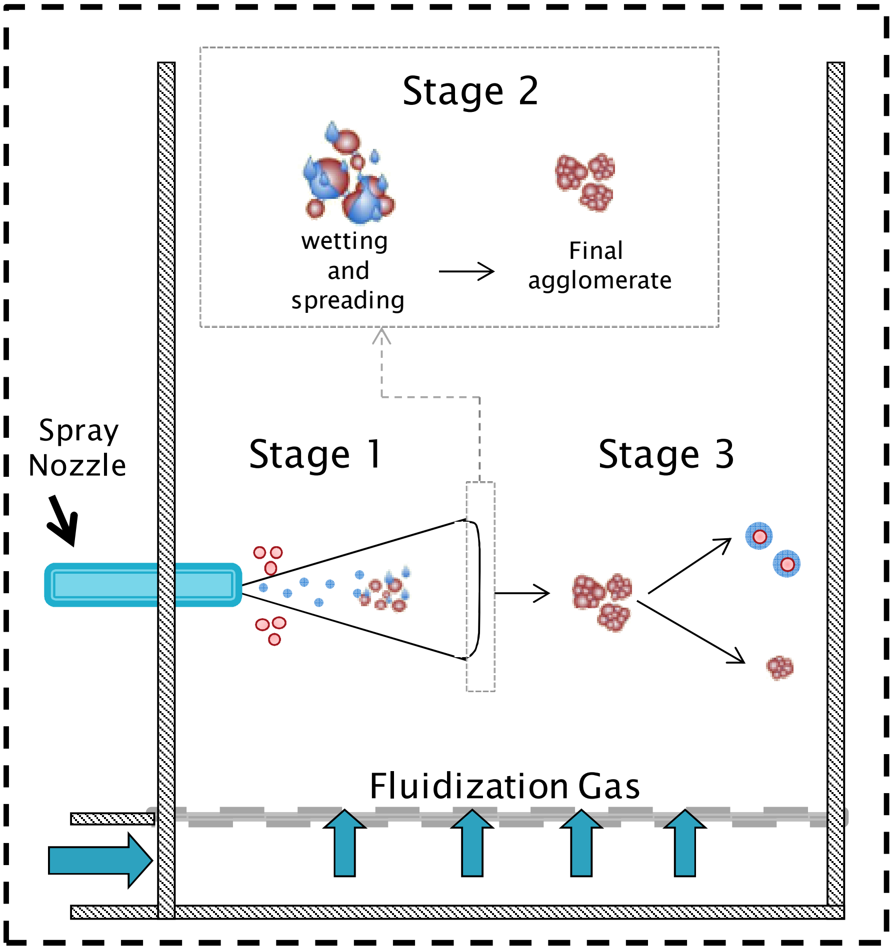

Figure 3-6: Mechanism for wet agglomeration in the Fluid Coking^{TM} process

The modified liquid solution used in this study has a lower viscosity than the one used in Chapter 2, which should result in the formation of smaller droplets from the spray nozzle and improve Stage 1, resulting in fewer agglomerates formed with lower liquid concentrations. The silica sand of the bed is less wettable by the solution, which should result in a lower total mass of agglomerates with a higher average liquid concentration from Stage 2. The impact of the new liquid solution on the liquid concentration of the agglomerates is, however, contradictory: the liquid concentration should decrease if Stage 1 predominates and increase if Stage 2 predominates. Agglomeration of silica sand particles was reduced by nearly 50 % for the new liquid solution with 5 % Plexiglas^{TM} (Figure 3-7), thus confirming the effect of liquid properties on the agglomeration tendency as reported by previews authors[14, 17]. This also agrees with the anticipated results.

Figure 3-8 shows that the effect of the new liquid solution on the liquid concentration in the agglomerates is complex: lower liquid concentrations were obtained in the macro-agglomerates (i.e: agglomerates with d_{aggl} > 600 µm) but larger liquid concentrations were obtained in the smaller, micro-agglomerates. Unlike the 10 % Plexiglas^{TM} system, where micro-agglomerates exhibit a much lower liquid concentration as compared to macro-agglomerates, the liquid concentration in micro-agglomerates for the 5% Plexiglas^{TM} system is not much different from the liquid concentration in the macro-agglomerates, which suggests that these agglomerates derive from the fragmentation of bigger agglomerates rather than from agglomerates initially formed at the tip of the jet cavity, in Stage 1. Furthermore, it can be observed from Figure 3-8 that the 5 % Plexiglas^{TM} system provides a more uniform liquid distribution, with a liquid concentration nearly independent of agglomerate size in macro-agglomerates. This is likely the result of the improved liquid spraying, with smaller droplets, that is obtained with a less viscous liquid. These results indicate that for the 5% Plexiglas^{TM} system, the effect of viscosity on the liquid distribution in Stage 1 predominates over the effect of wettability in stage 2.

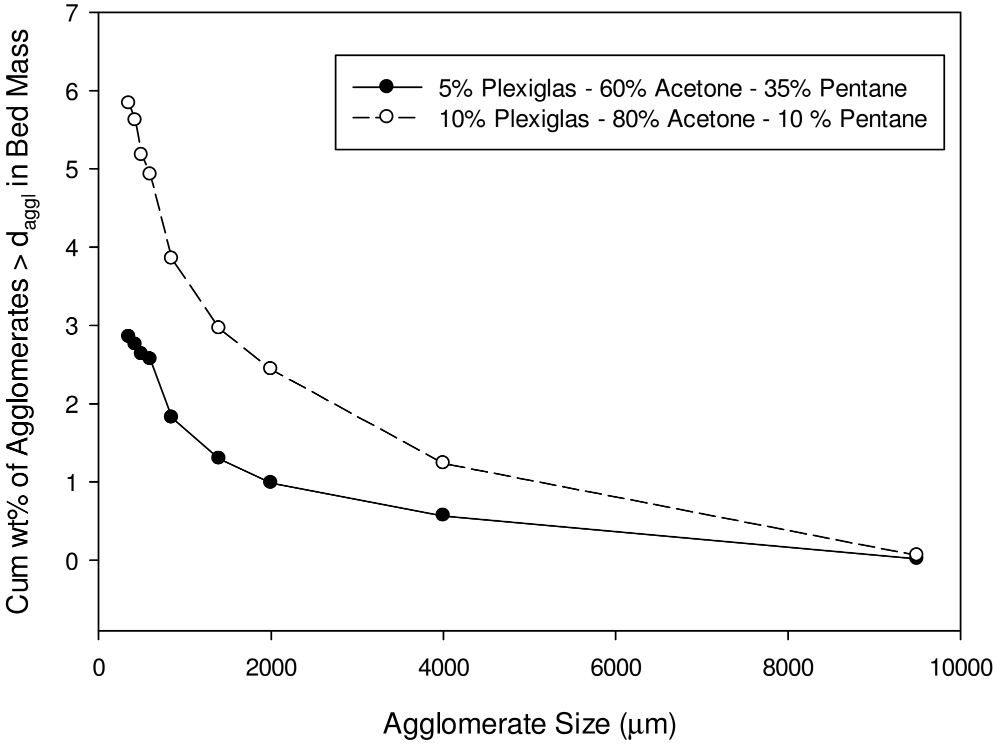

Figure 3-7: Effect of Liquid Properties on Agglomerate Formation

Furthermore, if a liquid mass balance is performed on recovered agglomerates; significant differences in liquid distribution can be observed between both systems. Figure 3-9 shows that with the 5% Plexiglas^{TM} system, about 40 wt% of the liquid injected is trapped in agglomerates with 60 wt% of the liquid available as free moisture on individual particles; with the 10 wt% Plexiglas^{TM} system, on the other hand, only 23 wt% of the liquid is available as free moisture with 74 wt% of the liquid trapped in agglomerates. The improvement on liquid – solid contact with the 5% Plexiglas^{TM} system is clear, since the larger and wetter agglomerates obtained with the 10% Plexiglas^{TM} system are most likely to create operating problems in the Fluid Cokers^{TM7}.

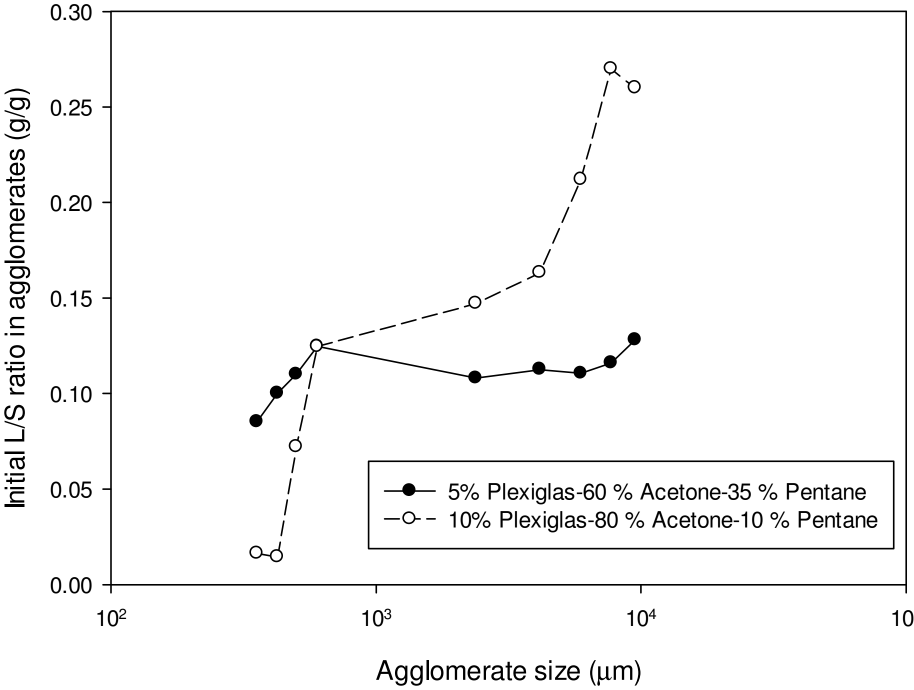

Figure 3-8: Effect of Physical Properties on Agglomerate Properties

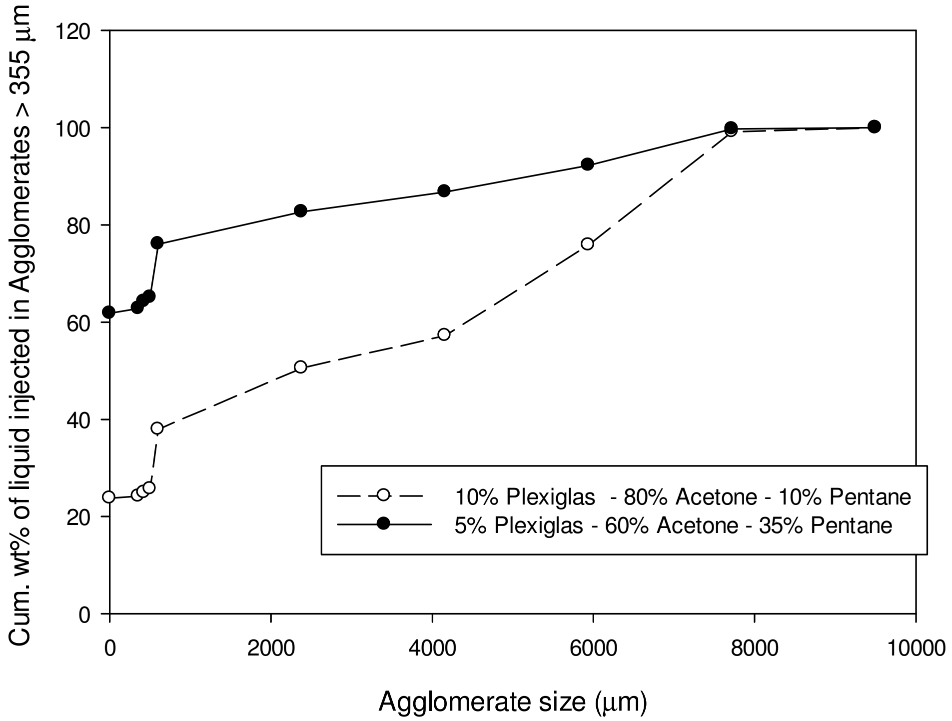

Figure 3-9: Effect of Physical Properties of the System on Liquid Distribution

3.3.2 Effect of Nozzle Design on Agglomerate Properties and Liquid Vaporization

3.3.2.1 Effect of Nozzle Attachment

In this section, experiments were performed with the TEB nozzle and the Clover Leaf attachment. The 10% Plexiglas^{TM} solution was selected for these experiments as it represents the worst case scenario, in terms of agglomerate formation and liquid distribution, as presented in section 3.2.1.

The Clover Leaf attachment has a higher impact on liquid distribution than on the mass of recovered agglomerates. Figure 3-10 shows the attachment has no significant impact on the size distribution of agglomerates. In order to confirm these results, additional experiments were conducted at higher GLR values, i.e. with more atomization gas. Figure 3-11 shows that, in all cases, the TEB nozzle without the attachment performs better. The error bars show the variability of the results obtained in two repeated runs. The error was not considered significant as to be shown for all the performed runs.

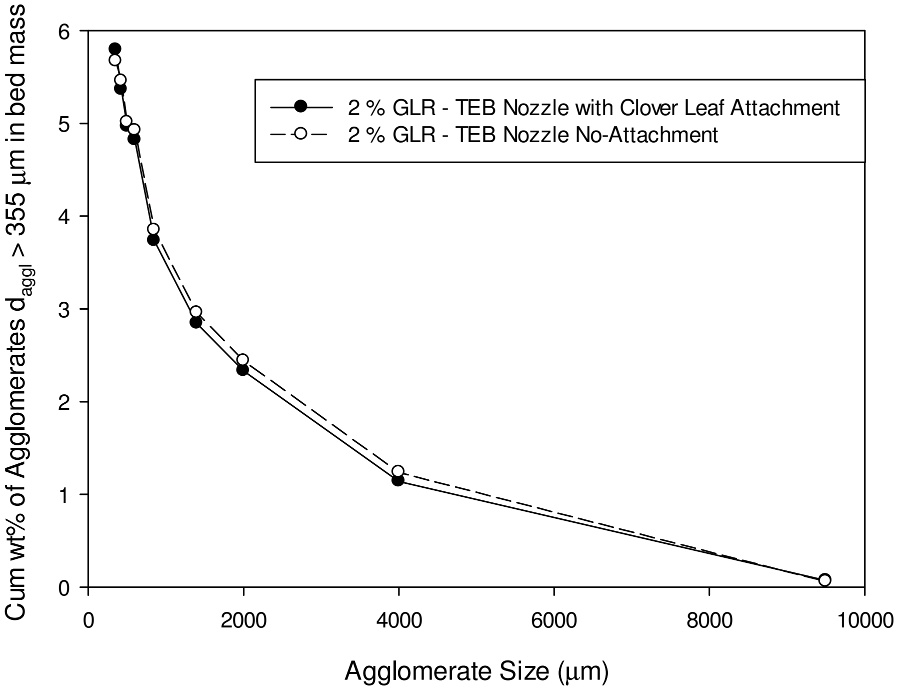

Figure 3-10: Effect of Nozzle Attachment on Agglomerate Formation for 2 w% GLR

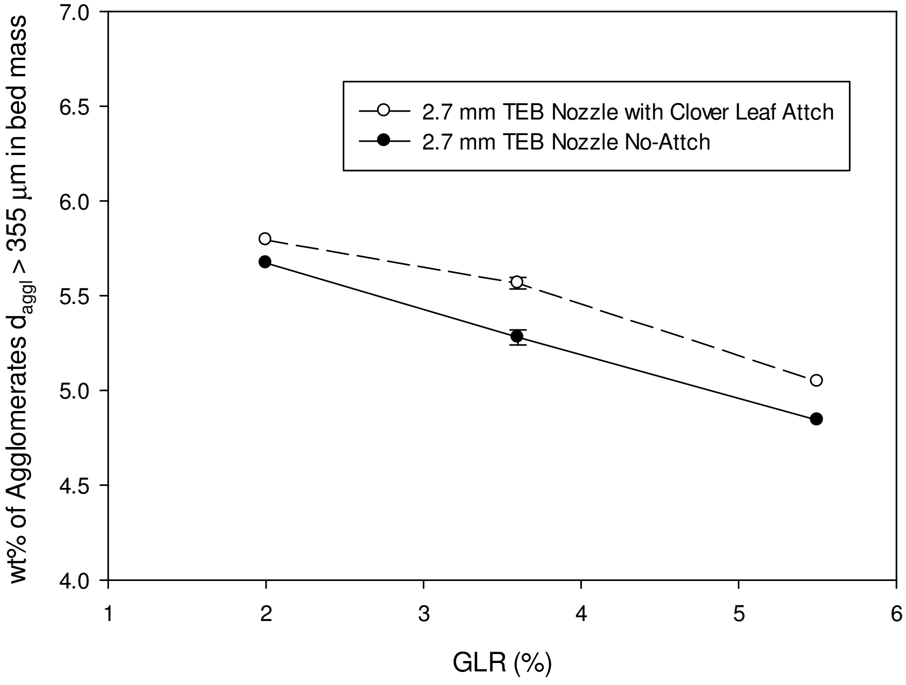

Figure 3-11: Effect of Nozzle Attachment for Different GLR

Figures 3-12 and 3-13 show the effect on the vaporization rate of the liquid. Both the dissipation time and the mass of residual liquid are increased when the Clover Leaf attachment is used, and this slower vaporization confirms the results obtained for the total mass of agglomerates, given the effect of agglomerates on liquid vaporization presented in Chapter 2.

Figure 3-14 shows that the Clover Leaf attachment produced slightly wetter agglomerates for most of the size cuts. As a result, a mass balance on the liquid recovered from the agglomerates indicates that having the Clover Leaf attachment reduces the quantity of liquid injected available as free moisture from 23 to 3 wt%, as presented in Figure 3-15. This also confirms the results obtained for the vaporization rate of the liquid, where the Clover Leaf attached slows down the vaporization rate of the liquid for all the tested conditions.

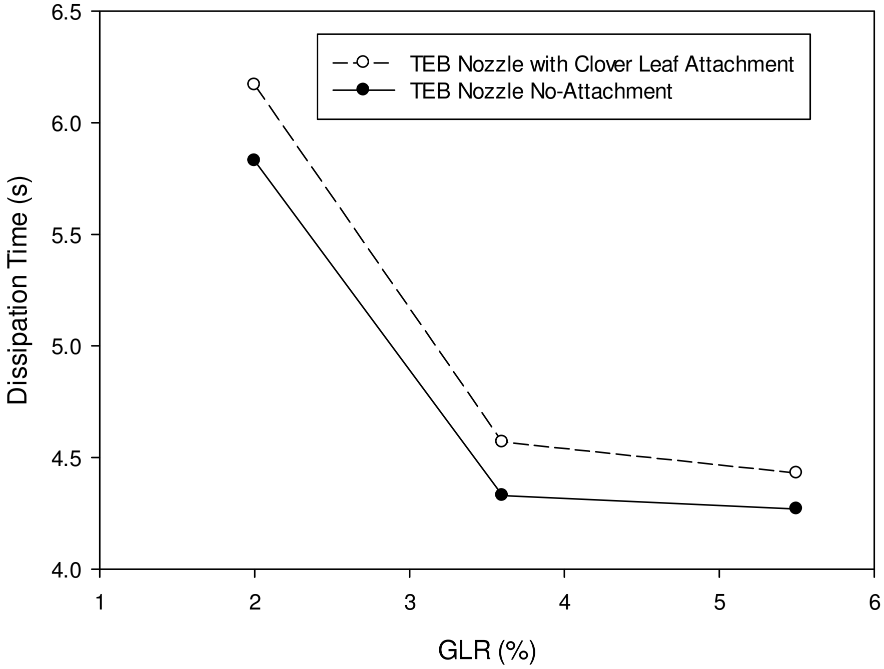

Figure 3-12: Effect of nozzle attachment on liquid vaporization (dissipation time)

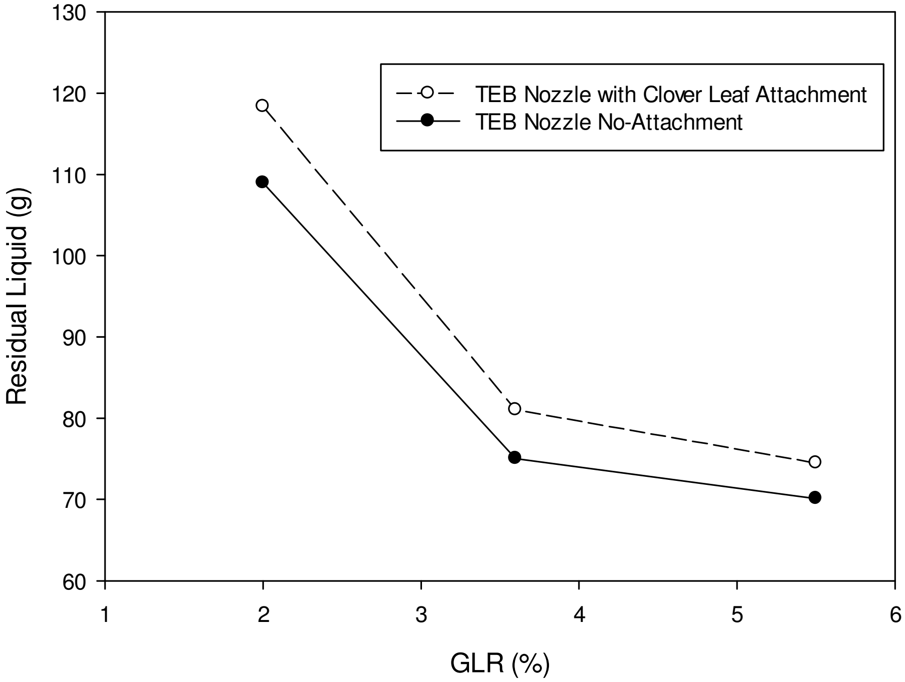

Figure 3-13: Effect of nozzle attachment on liquid vaporization (residual liquid)

Given the design of the nozzle attachment used in this study, it is expected that the gas-liquid jet issuing from the nozzle would have a larger expansion angle when the Clover Leaf attachment is used. These results seem to indicate that, according to findings from Pougatch et al.[13], a Clover Leaf attachment, such as the one used in this study, does not significantly destabilize the jet boundary to promote entrainment of solids and better mixing in the jet cavity. Further investigation is needed for other Clover Leaf designs in order to better improve the performance of these modified nozzles.

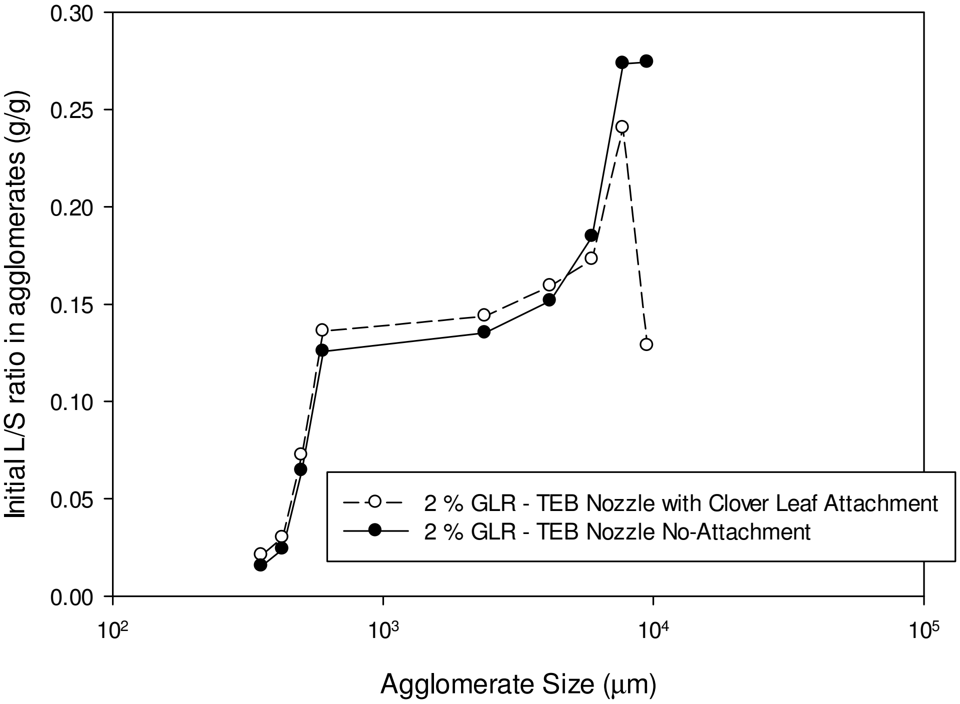

Figure 3-14: Effect of nozzle attachment on agglomerate properties

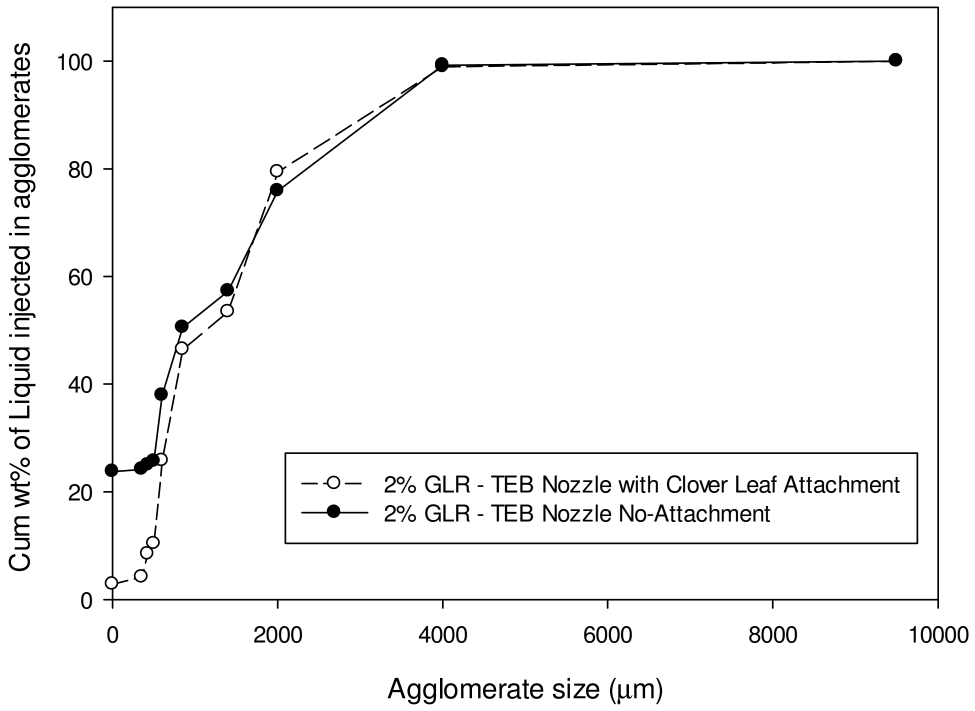

Figure 3-15: Effect of nozzle attachment on liquid distribution

3.3.2.2 Effect of Sonic Gas Jets

The use of sonic gas jets around the nozzle, referred to as "Satellite Nozzles" in this study, was first introduced by House et al.[9] and further studied by Saha et al.[10]. These authors found significant improvements in liquid distribution as well as a reduction on the formation of large agglomerates, responsible for significant heat and mass transfer limitations and operating problems in the Fluid Coking™ process. However, both studies were conducted using a liquid solution with a viscosity of 3 cP which falls within the higher range of values available in the literature for bitumen at injection conditions. Given the uncertainty of bitumen properties and the significant impact of liquid properties on agglomerate formation and liquid distribution, as presented in section 3.3.1, it is important to confirm the results obtained by previous authors when using the Satellite nozzles with a less viscous solution. Furthermore, the new experimental model proposed in Chapter 2 allowed for a study of the effect of this nozzle configuration on the vaporization rate of the liquid. In this case, the 5% Plexiglas™ solution was used as it provides the lowest viscosity and highest contact angle expected for the bitumen–coke system.

The present study tested the same Satellite Nozzles as used by Saha et al.[10]. The authors performed tests with various atomization gas flowrates and, in all cases, the use of Satellite Nozzles reduced the total mass of macro–agglomerates and increased the mass of micro-agglomerates. The present study intends to confirm these improvements with a different liquid, and uses only one atomization gas flowrate (i.e. 2 wt% GLR).

In agreement with results presented by Saha et al.[10], the mass of large agglomerates (d_{aggl} > 850 μm) was greatly reduced when using the Satellite nozzles (Figure 3-16), while the mass of smaller agglomerates (355 μm < d_{aggl} < 850 μm) was increased, as shown in Figure 3-17.

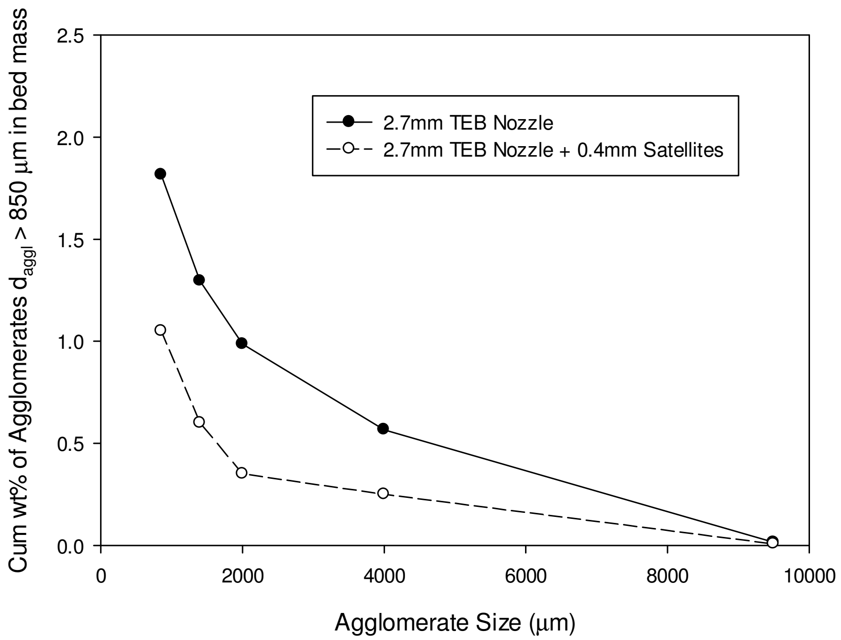

Figure 3-16: Effect of Satellite jets on macro-agglomerate mass

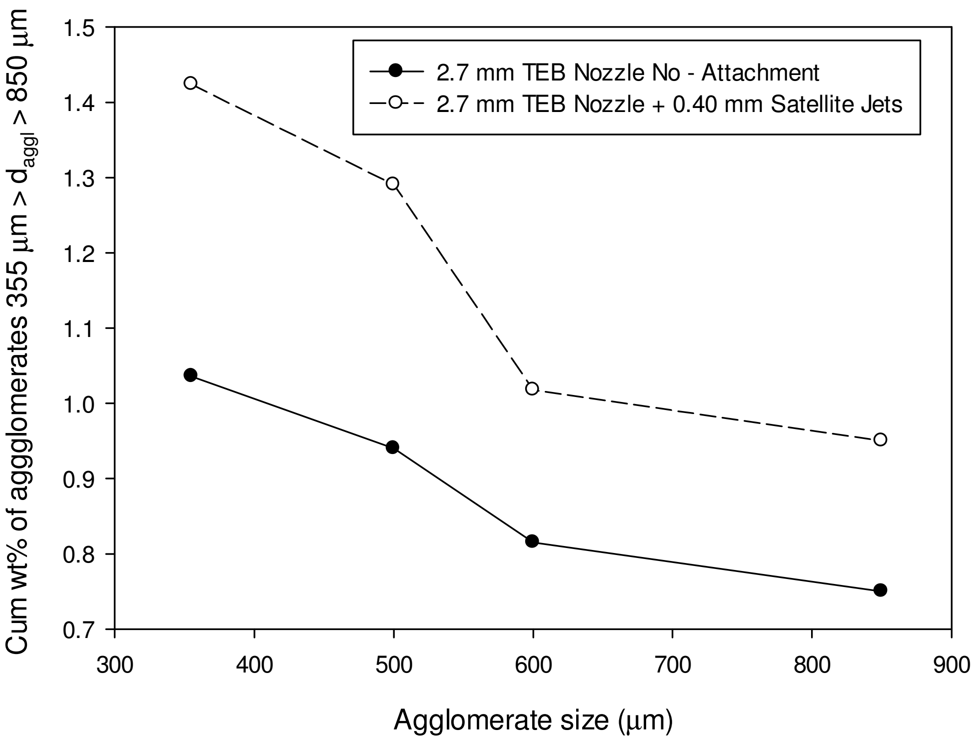

Figure 3-17: Effect of Satellite jets on micro-agglomerate mass

Unlike the results presented by House et al.[9], where all the agglomerates exhibited lower liquid concentrations when Satellite Nozzles were used, this study found that Satellite Nozzles did not significantly affect the liquid concentration of the large agglomerates ($d_{aggl} > 850$ µm), while greatly reducing the liquid concentration of smaller ones (355 µm $< d_{aggl} < 850$ µm) (Figure 3-18). As a result, Figure 3-19 shows that the Satellite Nozzles reduced the proportion of injected liquid trapped in agglomerates by about 10 wt%. This can lead to a significant improvement in the liquid yield of Fluid Cokers.

Satellite Nozzles, therefore, produce fewer macro-agglomerates. Although they produce more micro-agglomerates, they greatly reduce the liquid concentration of these agglomerates so that a lower proportion of the injected liquid is trapped in agglomerates. Satellite Nozzles are, therefore, expected to greatly improve the performance of Fluid Cokers™.

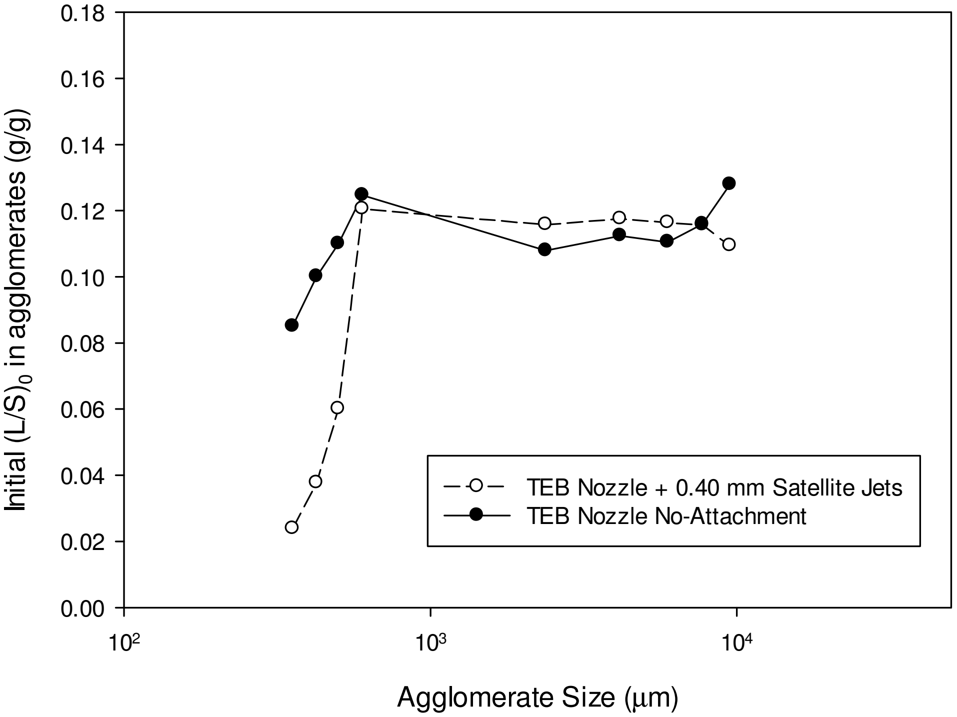

Figure 3-18: Effect of Satellite jets on agglomerate properties

The improved liquid distribution observed for the Satellite Nozzles did not have a significant impact on the vaporization rate of the liquid as shown on Table 3-2. However, an 8.3 % decreased was observed for the residual liquid when the Satellite Nozzle was used.

Table 3-2: Effect of Satellite nozzle on liquid vaporization

	Satellite Nozzle	**TEB Nozzle No-Attachment**
Dissipation time (s)	5.33	5.83
Residual Liquid (g)	74.44	81.18

In order to better understand the mechanism through which the Satellite Nozzles improve the liquid distribution for the micro-agglomerates (355 μm < d_{aggl} < 850 μm), the fraction of solids trapped in these agglomerates was reported as a function of the total mass of solids in the fluidized bed. It can be seen from Figure 3-20 that with the Satellite Nozzles, a much larger proportion of the bed solids is trapped in the micro-agglomerates. This explains the low liquid concentration for these agglomerates. This also confirms the suggestion from House et al.[9] that the improved performance of the Satellite Nozzles results from a higher entrainment of solids flux into the jet cavity and better mixing of liquid and solids within the jet cavity.

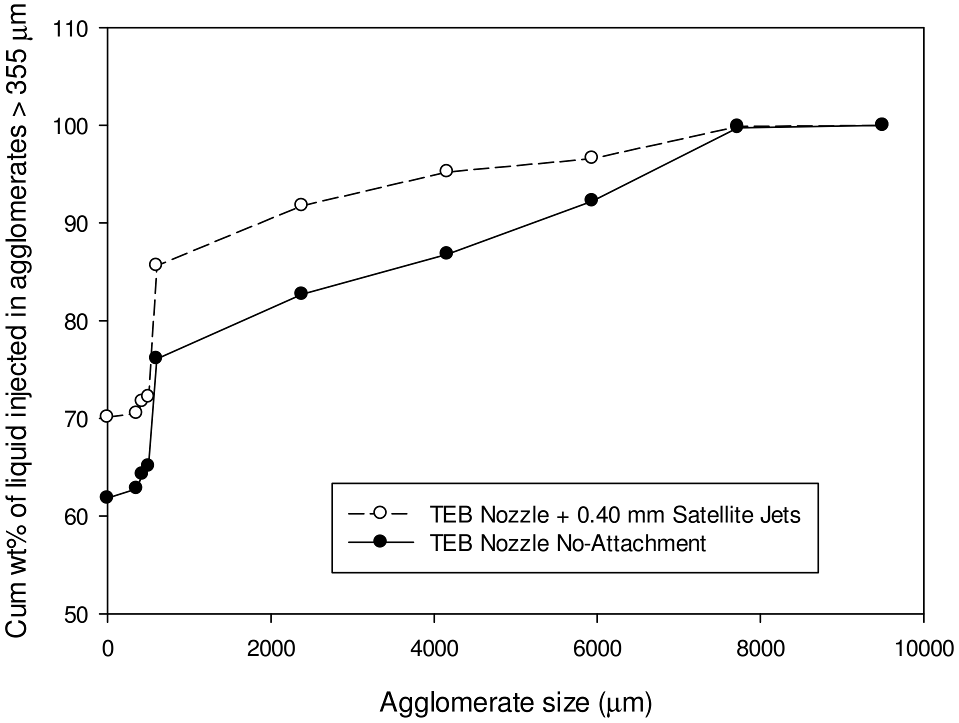

Figure 3-19: Effect of Satellite Nozzles on liquid distribution

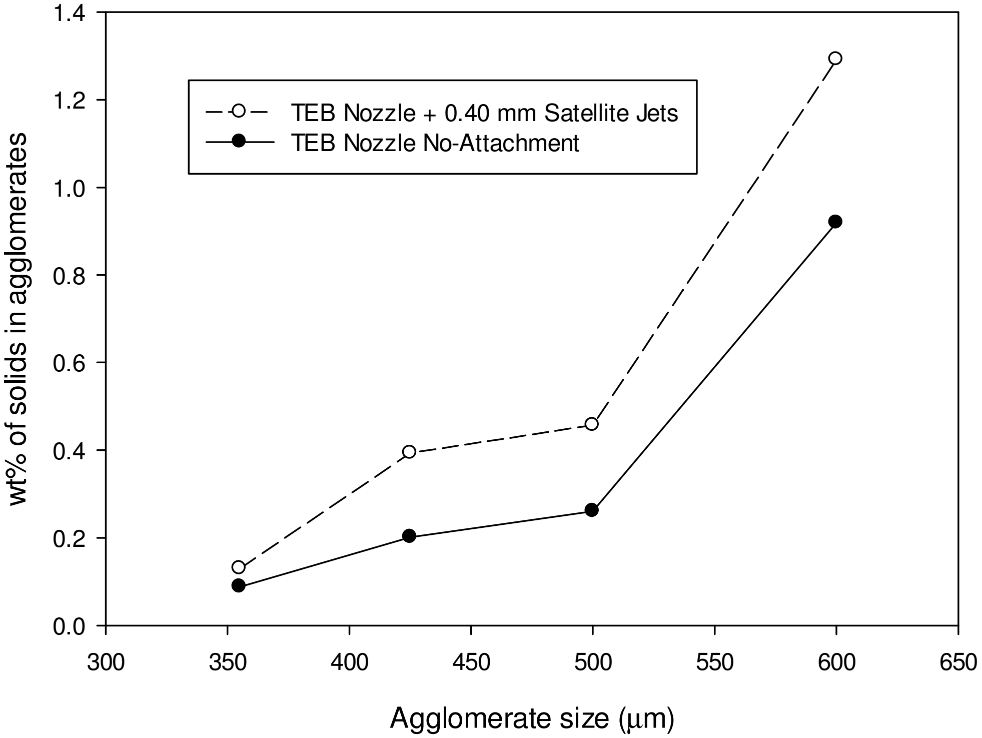

Figure 3-20: Effect of Satellite jets on solids entrainment

3.4 Conclusions

The effect of liquid properties on agglomerate formation and liquid distribution was studied by adjusting the viscosity and contact angle of liquid solution injected in a fluidized bed to match as much as possible the operating conditions relevant to the Fluid Coking^{TM} process. The following observations were made:

- Decreasing simultaneously the viscosity and the wettability of the system enhanced dispersion of the liquid on the surface of the particles and reduced the total mass of agglomerates formed by 50 %;
- Using a less viscous solution improved the performance of conventional TEB nozzle used in the Fluid Coking^{TM} process and enhanced initial liquid dispersion on the particles, evidenced by a narrower liquid concentration fluctuations among different agglomerate sizes;

- Decreasing the viscosity and wettability of the system decreased the strength of the large agglomerates ($d_{aggl} > 600$ μm), promoting the fragmentation of these agglomerates into smaller agglomerates with similar liquid concentrations.

Furthermore, the effect of spray nozzle design was studied by using two different modifications of the conventional TEB nozzle used in the Fluid Coking^{TM} process:

- A Clover Leaf attachment at the tip of the conventional TEB nozzle increased the total mass of agglomerates formed for all conditions tested;
- With a Clover Leaf attachment, slightly more liquid is trapped in agglomerates, resulting in a lower quantity of liquid available as free moisture on individual particles;
- The Clover Leaf attachment reduces the vaporization rate of the liquid, which confirms the higher mass of wetter agglomerates obtained with this nozzle;
- Using a spray nozzle with Satellite gas jets (Satellite Nozzle) results in fewer macro-agglomerates and drier micro-agglomerates;
- The Satellite jets enhance solids entrainment from the fluidized bed into the jet cavity, resulting in agglomerates with lower liquid concentrations;
- The results obtained in this study for the Satellite Nozzles corroborate findings from previous authors. Since the benefits of the Satellite Nozzles have been confirmed for a wide range of liquid properties, similar improvements can be expected for the bitumen–coke system.

3.5 References

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Chapter 4

4 Effect of Bed Hydrodynamics and Vaporization Rate on Agglomerate Properties

4.1 Introduction

Many industrial fluidized units involve the injection of reactants or liquid binders in the form of droplets through specially designed spray nozzles. In applications such as the Fluid Coking^{TM} process, optimum contact of liquid droplets and the fluidized particles is crucial to prevent the formation of agglomerates with high liquid contact, which are responsible for heat and mass transfer limitations in the thermal cracking or coking of heavy hydrocarbon compounds from the bituminous feed[1].

In Chapter 3, a review of the literature on Fluid Coking^{TM} and the injection of liquids in fluidized beds led to the following general mechanism for the formation of agglomerates in the Fluid Coker, which involves three stages:

1. Initial distribution of liquid sprayed in the form of fine droplets among entrained particles in the jet cavity;
2. Wetting and distribution of the liquid on the surface of the particles;
3. Break-up of agglomerates due to shaear forces and destabilization of the wet agglomerates, as a result of constant cracking and devolatilization of the product.

Experimental studies on jet-bed interaction have found that the formation of agglomerates in stage 2 typically happen at the tip of the jet cavity, at a certain distance from the nozzle exit, and is highly dependent on mixing and liquid distribution in stage 1[2, 3].

Bed hydrodynamics can have a significant impact on stage 1. Pougatch et al.[4] developed a numerical model to describe liquid-solid contact and jet-bed interactions in a fluidized bed under conditions relevant to the Fluid Coking^{TM} process. This model predicted that a higher fluidization velocity should improve bed mixing and liquid distribution in the jet cavity. It also predicted that the jet region in the vicinity of the nozzle exit should not be affected by bed hydrodynamics which confirmed measurements obtained by Hulet et al.[5] showing that the fluidization velocity did not greatly affect the entrainment of solids from the bed into the jet regions near the nozzle tip. The model from Pougatch et al.[4] predicted, however, that the fluidization velocity should affect the jet cavity at distances farther from the nozzle exit, where agglomerates are expected to be formed. Mohagheghi et al.[6] confirmed that higher fluidization velocities can reduce the formation of agglomerates during liquid injection. Similarly, higher fluidization velocities have been found to reduce agglomerate formation in fluidized spray granulation processes, which has been attributed to a higher impact energy that must be absorbed by the liquid binder upon collision thus decreasing the probability of successful collisions[7]. Although the agglomerating mechanism in fluidized spray granulation processes was initially believed to be consistent with the one encountered in the Fluid Coking^{TM} process[8], recent studies have shown that in the Fluid Coking^{TM} process, most of the injected liquid is initially trapped in wet agglomerates[6], while in fluidized spray granulation processes, the objective is to coat individual particles with liquid, with these individual particles then agglomerating with dry particles in the bulk of the fluidized bed.

Bed hydrodynamics can also have a significant impact on stage 3, the break-up of agglomerates in the bulk of the fluidized bed. Weber et al.[9] demonstrated that the level of fragmentation and erosion of agglomerates is a complex phenomenon dependent on different factors, such as fluidization velocity, initial agglomerate size, liquid concentration in the agglomerates and physical properties of the liquid binder. They found that increasing the fluidization velocity accelerated agglomerate break-up. Mohagheghi et al.[6] developed a new measurement technique for to study the stability of agglomerates formed with spray nozzles that were scaled down from the nozzles as used in industrial Fluid Cokers^{TM}; they confirmed that increasing the fluidization velocity accelerated agglomerate break-up.

In the Fluid Coking^{TM} process, breakage of the agglomerates in stage 3 will ideally result in smaller fragments with a liquid film from which cracking and devolatilization of the product take place. Bruhns et al.[10] showed that, even when the unit is operated at temperatures above the boiling point of the injected liquid, no instantaneous evaporation occurs before the liquid droplets contact individual particles and there is initial formation of wet agglomerates. Li et al.[11] developed a numerical model to simulate liquid vaporization in the Fluid Coking^{TM} process and predicted a significant impact of the vaporization rate of the liquid on local bed hydrodynamics, thus affecting the liquid-to-solid ratio in the fluidized bed. However, their model did not consider changes in temperature due to liquid vaporization and the agglomeration phenomena which can also affect the vaporization kinetics.

In this Chapter, the new experimental model presented in Chapter 1 is used to study the effect of bed hydrodynamics and liquid vaporization rate on the properties of agglomerates formed when liquid is injected in a fluidized bed, under conditions relevant to the Fluid Coking^{TM} process. The results obtained are expected to provide a better understanding of the effect of process conditions (e.g. fluidization velocity, operating temperature) on the agglomeration mechanisms proposed by previous authors and summarized in Chapter 3.

4.2 Experimental Set-up and Methodology

Experiments were performed in a large scale fluidized bed with a rectangular cross section of 1.2 m by 0.15 m and an expansion zone with a section of 1.2 m by 0.47 m at a height of 1.5 m from the ground (Figure 4-1). The unit was operated with 150 kg of silica sand particles with a Sauter mean diameter of 210 μm. Two nitrogen lines supplied gas for fluidization and each line was equipped with a sonic nozzle to control the mass flowrate of nitrogen required for a desired superficial gas velocity. Electric heaters in each nitrogen line were used to maintain a desired temperature in the fluidized bed. The unit was equipped with two cyclones in series, and the first cyclone recycled its collected fines to the bed through a dipleg, while the fines collected by the secondary cyclone were recovered externally.

In this study, the modified form of the liquid solution introduced in Chapter 3 was used, and its physical properties are presented in Table 4-1. According to the results obtained in Chapter 3, agglomerates formed with this solution fragment more easily. It is then expected that this system (i.e. 5 wt% Plexiglas^{TM} solution) will be more susceptible to the changes in the operating conditions to be made in this study.

The solution at ambient temperature was injected horizontally in the dense fluidized bed, 0.38 m above the distributor plate at 30 g/s for 42 s. This injection time was selected to reach steady-state evaporation and produce enough agglomerates to guarantee reproducible results. In order to achieve this liquid flowrate, the pressure on the liquid tank, shown as P2 on Figure 4-1, was adjusted by regulating the pressure of nitrogen from the main line. In this study, a scaled down version of an industrial nozzle used in the Fluid Coking^{TM} process, known as a TEB nozzle[11], was employed with an internal diameter of 2.7 mm using nitrogen at ambient temperature for atomization. In this case, the pressure on the atomization line, shown as P1 on Figure 4-1 was adjusted to obtain a specific atomization gas flowrate, expressed as GLR, or Gas-to-Liquid Ratio (wt/wt).

The bed was kept fluidized at minimum fluidization conditions for 10 min after liquid injection in order to dry the bed while preserving the initial size distribution of the agglomerates. One sample port at the bottom of the unit allowed for recovery of the bed mass along with the agglomerates for further processing. Then, the bed mass was classified into three major groups:

- Macro – agglomerates: agglomerates recovered from the bed mass after injection with a diameter $600\ \mu m < d_{aggl} < 9500\ \mu m$
- Micro – agglomerates: agglomerates recovered from the bed mass after injection with a diameter $355\ \mu m < d_{aggl} < 600\ \mu m$
- Individual bed particles: particles with a diameter below 355 μm

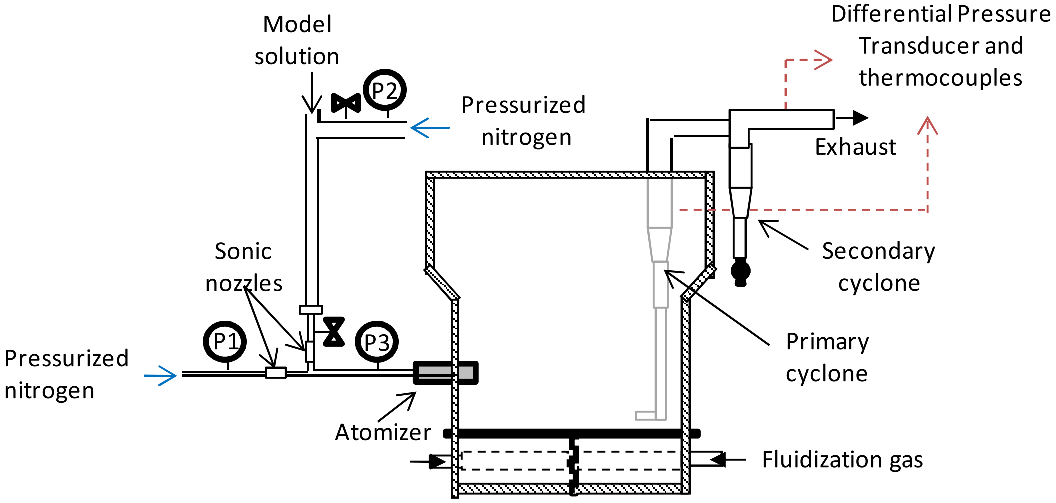

Figure 4-1: Schematic representation of the large scale fluidized bed

Table 4-1: Physical Properties of Model Solution (5% Plexiglas^{TM}-60% acetone-35%pentane)

	Syncrude AVR (400°C)	Model Solution (21°C)
Surface Tension (mPa.s)	21[4]	19.46
Initial viscosity (cP)	1 – 2[7]	0.80
Solid particles (d_{psm})	135 µm	210 µm
Contact Angle (°)	Not Available	45

Macro-agglomerates were recovered by sieving the entire bed mass with the desired sieve size, since there were no initial particles with a diameter greater than 600 µm. The Plexiglas^{TM} concentration in these agglomerates was obtained by breaking up the agglomerates and using a Soxhlet extraction apparatus with acetone as a solvent to dissolve the Plexiglas^{TM} binder. Gravimetric analysis of the sample using a balance with an accuracy of 0.1 mg provided the mass of Plexiglas^{TM} that had been dissolved. In order to determine the dissolution time required to completely dissolve the Plexiglas^{TM} in the agglomerates, the samples were re-processed until no difference in the mass of the sample was observed. In addition, analysis with a Halogen moisture analyzer of the solvent recovered in subsequent washes verified that no dissolved Plexiglas^{TM} was present. Once the amount of Plexiglas^{TM} in the original solids sample had been determined, the amount of liquid initially trapped in the agglomerates was calculated by mass balance, knowing the initial concentration of Plexiglas^{TM} in the injected liquid.

On the other hand, the size of micro-agglomerates falls within the size range of individual particles originally in the silica used for these experiments. Then, fines trapped in these agglomerates were used as tracers to estimate the total mass of micro-agglomerates formed during the injection. In this case, once the bed mass had been sieved to recover macro-agglomerates, a representative sample from the bed mass below 600 μm was taken and processed with the same Soxhlet extraction apparatus described above. Particle size distribution of this sample was obtained using a laser diffraction method (HELOS of Sympatec), which provided information on the concentration of fines that were released upon dissolution of the liquid binder. This, along with the mass of Plexiglas^{TM}, allowed estimation of the total mass of micro-agglomerates in the sample. Detailed calculation used for this analysis can be found in Chapter 1.

Finally, differential pressure measurements between the freeboard and the exit of the secondary cyclone were taken during the injection and the drying period. A flow model was then used to estimate the rate of injected liquid being vaporized in the bed. Major assumption of this model included:

- Ideal gas behavior. This allowed determination of the total number of moles in the freeboard, including nitrogen and solvent vapors
- Cyclone pressure drop is proportional to the product of the square of the gas molar flowrate and its molecular weight
- Plug flow of gas in freeboard

Detailed equations used in this model can be found in Chapter 1.

4.3 Results and Discussion

4.3.1 Effect of Fluidization Velocity on Agglomerate Properties

Experiments were conducted at a set fluidized bed temperature of 68 °C. The pressure in the nitrogen line used for fluidization was adjusted to obtain a superficial gas velocity of 0.20, 0.30 or 0.40 m/s in the bottom section of the bed.

Figures 4-2 and 4-3 show that increasing the fluidization velocity decreased the mass of macro-agglomerates while increasing the mass of micro-agglomerates. As expected, increasing the fluidization velocity enhances the fragmentation of the particles into smaller agglomerates, in agreement with results from previous authors[6, 8]. Weber et al.[8] showed that the fluidization velocity has a significant impact on the breakage mechanism of agglomerates, which can also be affected by other factors such as liquid properties and initial agglomerate size. It was observed that bigger agglomerates can be fragmented into more pieces that could undergo subsequent erosion thus resulting in a higher mass loss than smaller agglomerates.

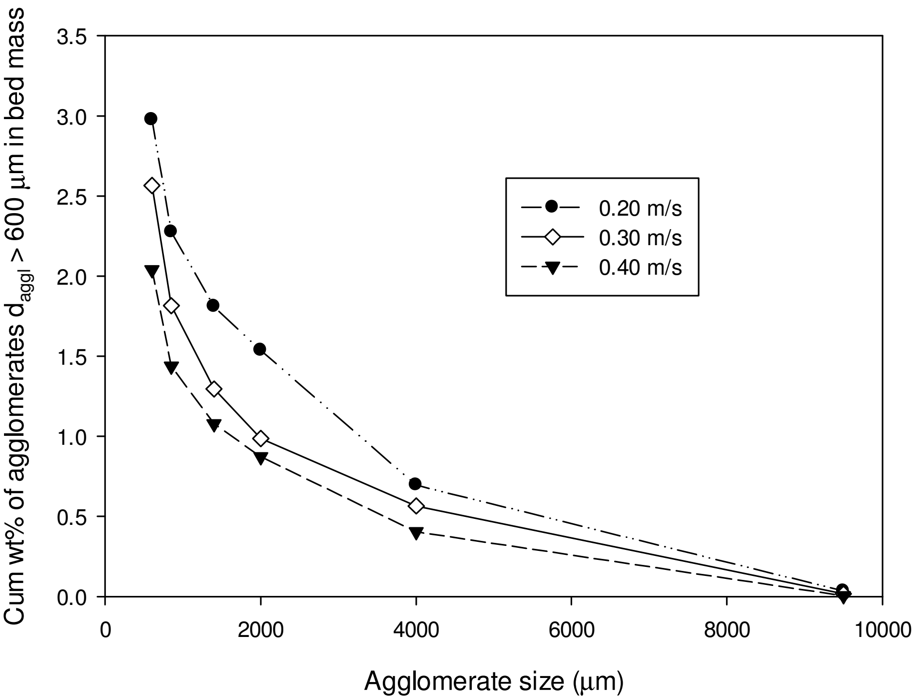

Figure 4-2: Effect of fluidization velocity on the formation of Macro-Agglomerates

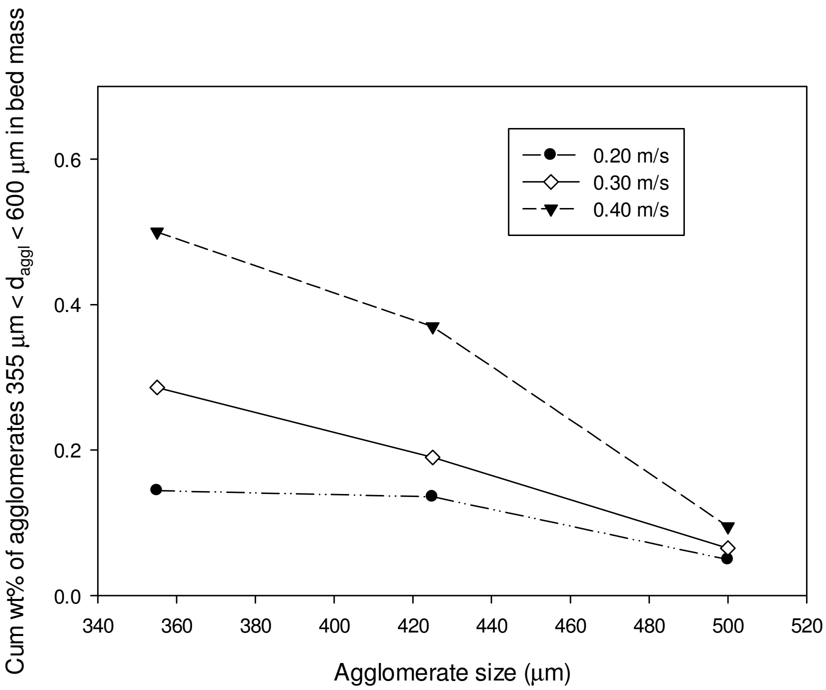

Figure 4-3: Effect of fluidization velocity on the formation of Micro-Agglomerates

When the agglomerate break-up in stage 3 is enhanced, the agglomerates that survive must be stronger, i.e. with a higher liquid concentration; in contrast, lower liquid concentrations were observed for agglomerates with $d_{aggl} > 2000$ µm, as shown in Figure 4-4. These results indicate that increasing the fluidization velocity not only favors break-up in stage 3 of the agglomerating mechanism, but can also improve initial liquid distribution on the particles in stage 1, which can also be confirmed from Figure 4-5 where increasing the fluidization velocity from 0.20 to 0.40 m/s decreased the total mass of liquid injected that is trapped in agglomerates by ~25%. This can be attributed to higher instabilities of the jet boundary caused by the bed turbulence due to a higher bubble frequency for higher fluidization velocities, resulting in better mixing in the jet cavity as reported by Pougatch et al.[5] Furthermore, in agreement with these authors, the improvement on liquid distribution becomes less significant as the fluidization velocity is increased beyond a certain value.

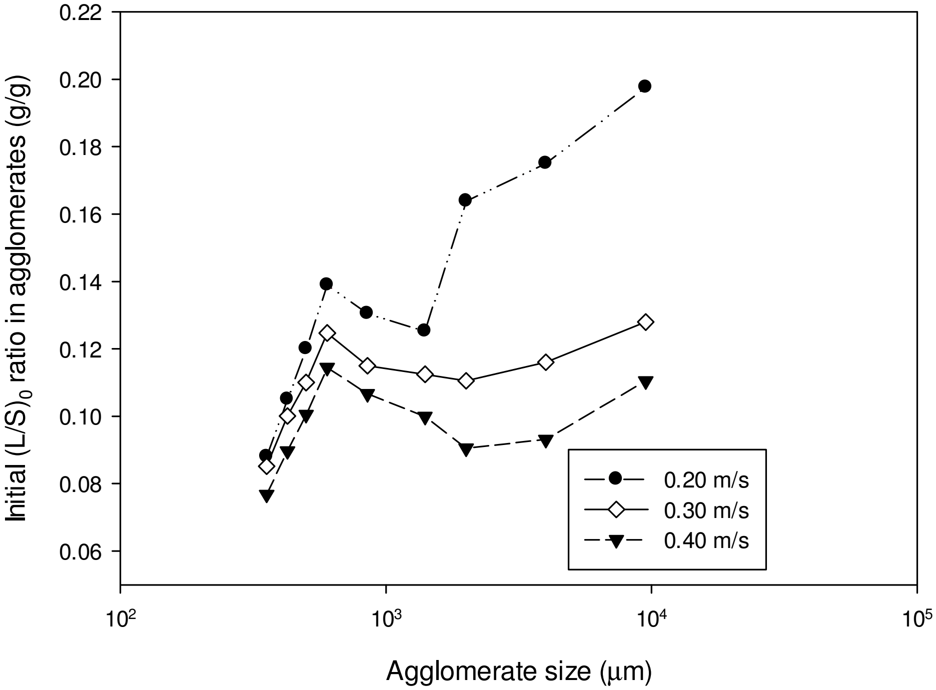

Figure 4-4: Effect of fluidization velocity on the initial liquid concentration in the surviving agglomerates

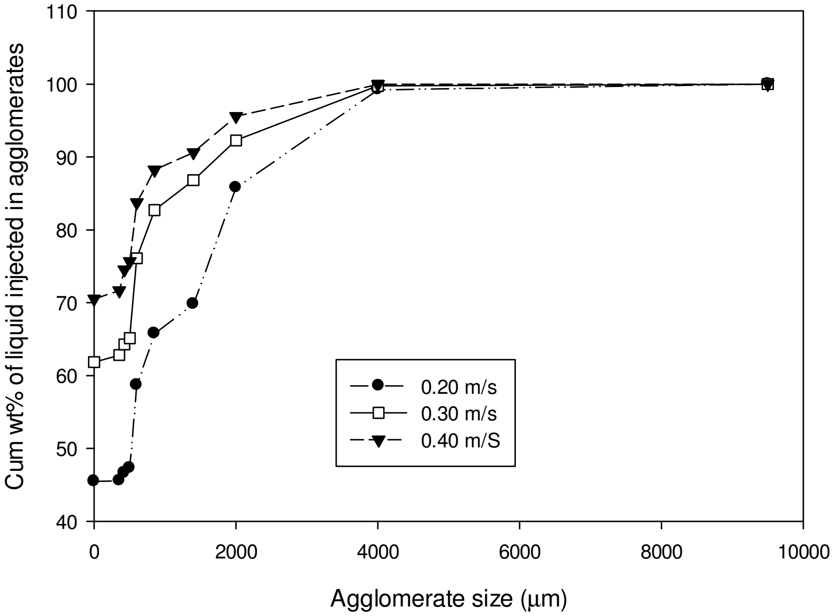

Figure 4-5: Effect of fluidization velocity on liquid distribution

4.3.2 Effect of Vaporization Rate on Agglomerate Properties

The vaporization rate of the liquid was increased by increasing the temperature of the fluidized bed from 68 °C to 88 °C, for all the superficial gas fluidization velocities tested in the previous section, while keeping all other conditions constant (e.g. GLR and liquid flowrate). Increasing the bed temperature reduces the dissipation time (Figure 4-6), as expected, due to the increased rate of evaporation of the liquid from the wet agglomerates. Accordingly, the total mass of agglomerates $d_{aggl} > 600$ μm recovered in these experiments was reduced as presented in Figure 4-7. In order to further study the mechanisms involved in such reduction, a fluidization velocity of 0.30 m/s was selected as a base case for additional analysis.

Figure 4-8 shows macro-agglomerates $d_{aggl} > 600$ μm recovered when the fluidized bed temperature was increased from 68 °C to 88 °C at a fluidization velocity of 0.30 m/s. The bed temperature was then further increased to 98 °C, however, no significant difference was observed with respect to the results obtained for the 88 °C experiments and this case was no longer considered in this study.

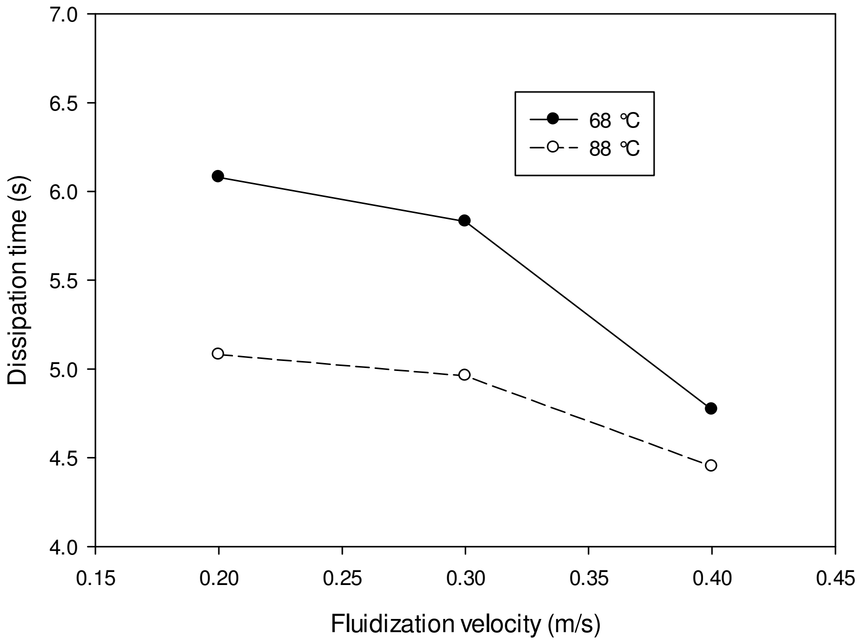

Figure 4-6: Effect of fluidized bed temperature on liquid vaporization

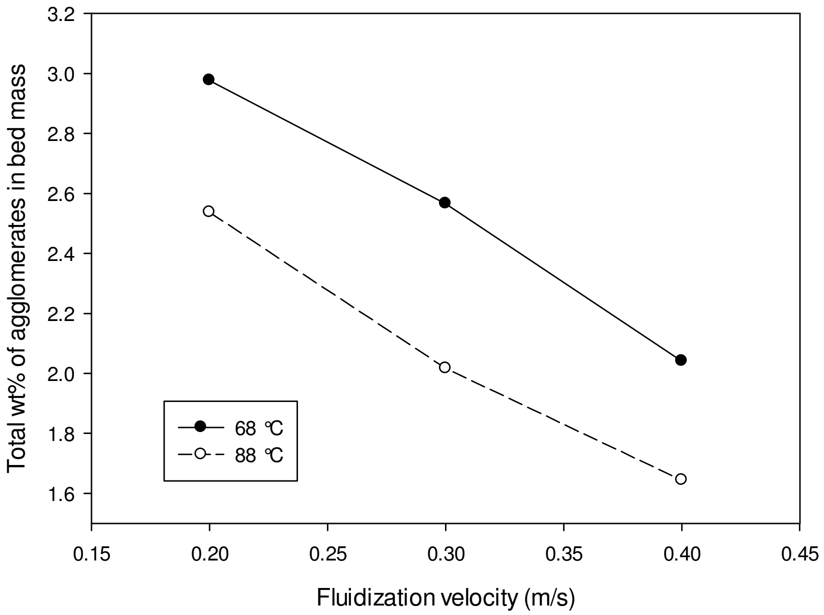

Figure 4-7: Effect of fluidized bed temperature on agglomerate formation

Agglomerates of the same size and initial liquid concentration, will dry faster at a higher temperature as shown in Figure 4-6. On the other hand, similarly to what has been observed for the viscosity of bitumen at reacting conditions[12], as the solvent in the Plexiglas™ solution evaporates, the liquid viscosity increases and the liquid bridges holding the particles in the agglomerates become stronger. Weber et al.[8] demonstrated that agglomerates made with a more viscous liquid were stronger.

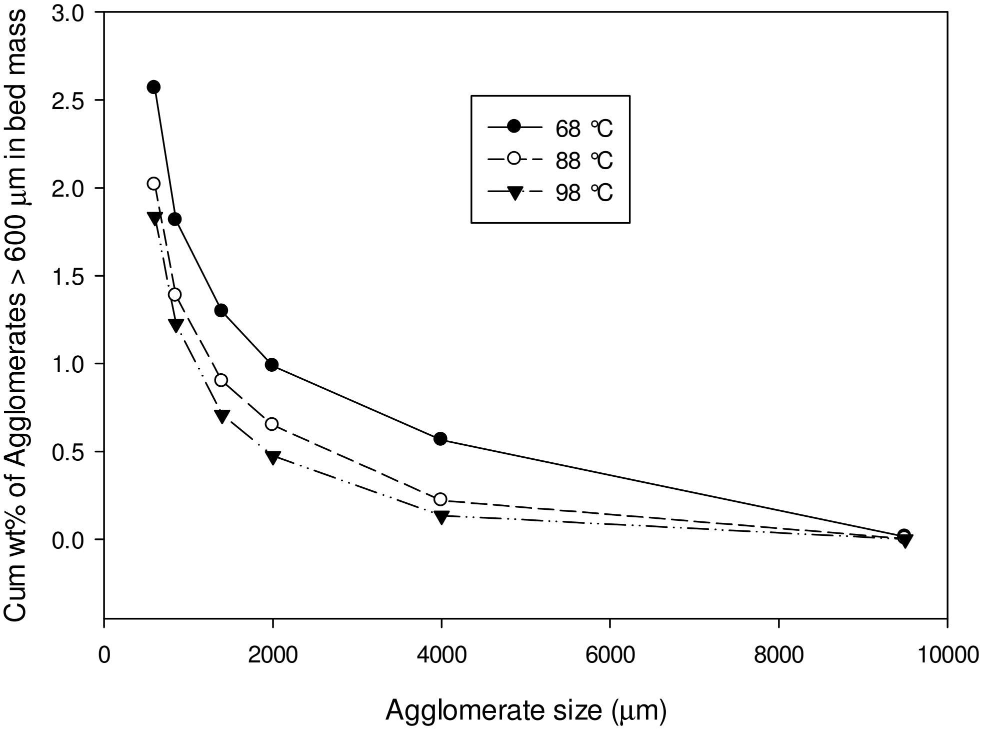

Figure 4-8: Effect of bed temperature on total mass of Macro-Agglomerates recovered

The effect of the bed temperature is primarily to change the drying rate of the agglomerates *d(L/S)/dt*, since they will get exposed to the same breakage rate *(dA/A$_o$)/dt*, regardless of the bed temperature. To more clearly isolate the important trends, a simplified general expression for the fraction of agglomerates that are broken is given:

$$\frac{A_0 - A_f}{A_0} = \int_{\left(\frac{L}{S}\right)_0}^{\infty} \left(\frac{\frac{dA}{A_0}}{dt} \right) \times \frac{dt}{d\left(\frac{L}{S}\right)} d\left(\frac{L}{S}\right) \qquad (4.1)$$

Where A_0 is the initial concentration of agglomerates in the bed and A_f is the final concentration. As the bed temperature increases, the drying rate increases and the proportion of agglomerates that break-up decreases (i.e. agglomerates have less time to decrease their liquid concentration and become weaker). This is the opposite of what was observed (Figure 4-8). Another factor must, therefore, predominate.

When the bed temperature increases, the temperature of the particles trapped in wet agglomerates formed at the tip of the jet cavity, in Stage 1, is higher. Because the liquid surrounding the small individual particles within the agglomerates reach thermal equilibrium quickly with the small particles, the liquid within the agglomerates is at a higher temperature and its initial viscosity is therefore lower. As shown earlier, everything else being equal, a lower liquid viscosity weakens agglomerates, making them more likely to be broken up. This is the predominant mechanism that explains the results of Figures 4-8 and 4-9.

On the other hand, Figure 4-10 shows that increasing the bed temperature also reduced the initial liquid concentration in the surviving agglomerates. If a heat balance is performed within the jet cavity, the following equation results:

$$m_{lv}\Delta H_v^* = m_s C_{p_s}\Delta T \qquad (4.1)$$

where the left-hand side of this equation represents the heat needed to vaporize the liquid, while the right-hand side represents the heat provided by the silica sand particles, being ΔT the temperature difference between the solid particles and the boiling point of the liquid. Then, the fraction of liquid vaporized is given by Equation (4.2):

$$\frac{m_{lv}}{m_l} = \frac{m_s}{m_l}\frac{C_{p_s}\Delta T}{\Delta H_v^*} \qquad (4.2)$$

where the term ΔH^* includes the energy required to heat up the liquid to its boiling point and the latent heat of vaporization. Studies on solids entrainment in a horizontal jet under conditions similar to this work suggest that the ratio of the solids entrainment flux to the liquid flowrate in the jet cavity is around 2.5[5]. Then, applying Equation 4.1 to the conditions used in this work, the fraction of liquid vaporized increased from 5 to 12 wt% when the bed temperature was increased from 68 to 88 °C. The total volumetric flowrate of gas and vapors through the jet cavity, therefore, increases by 73 %. This enhances the mixing between particles and liquid droplets within the jet cavity, resulting in agglomerates with lower liquid concentrations, as shown by Figure 4-10. Therefore, increasing the bed temperature results in a higher fraction of injected liquid that is available for distribution on individual particles (i.e. higher free moisture), and in small agglomerates, as shown in Figure 4-11.

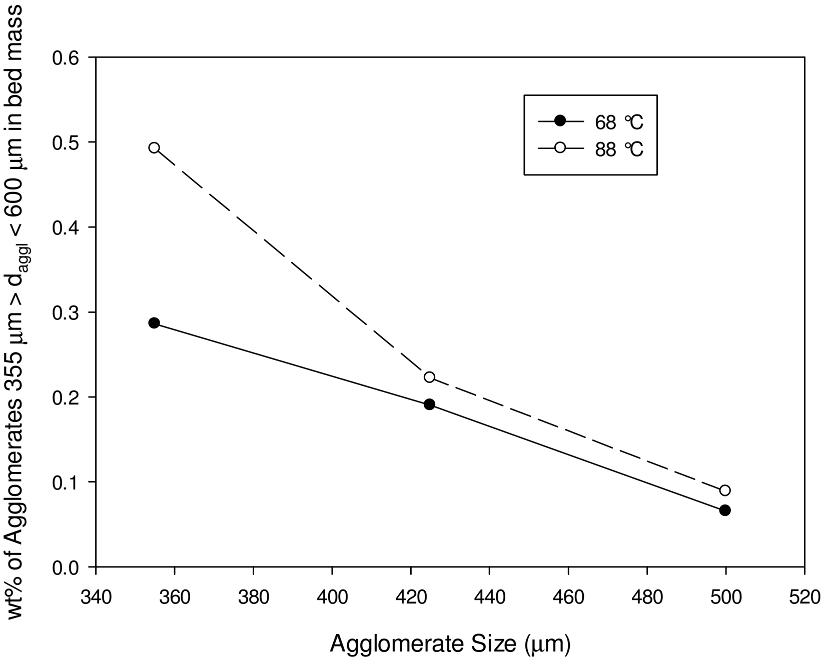

Figure 4-9: Effect of bed temperature on total mass of micro-agglomerates recovered

In a Fluid Coker™, most of the injected liquid must first crack before it can vaporize. According to Li et al.[10], the actual proportion of the injected liquid that will vaporize within the jet cavity is unknown, but some vaporization is expected. The results of this study therefore suggest that a higher coker temperature would have a beneficial impact on liquid distribution. However, further implications on the process when the operating temperature is increased must be considered, such as overcracking and reducing liquid yields.

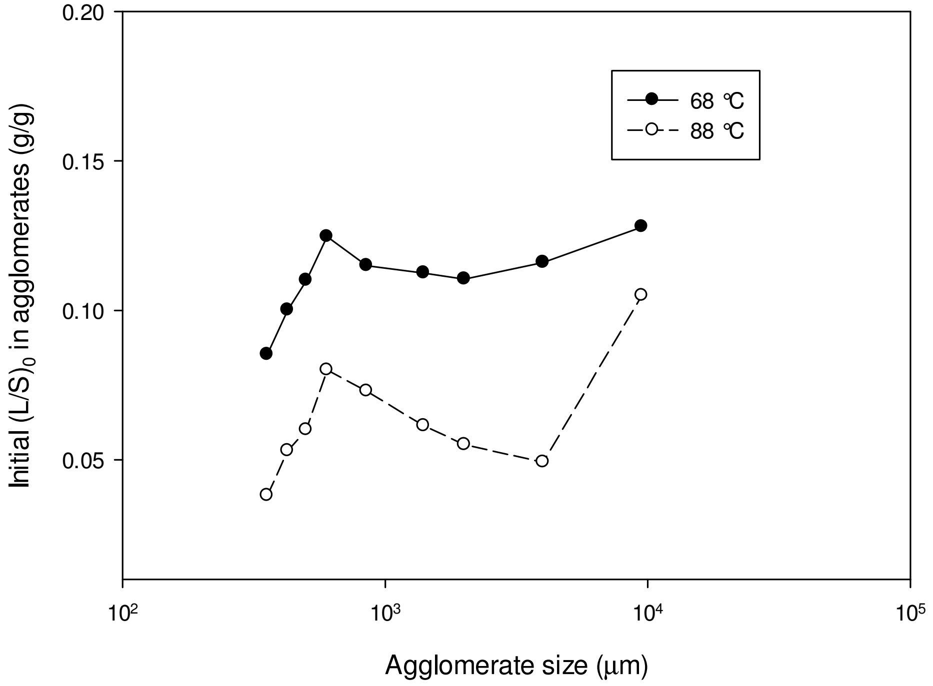

Figure 4-10: Effect of liquid vaporization on the initial liquid concentration in the surviving agglomerates

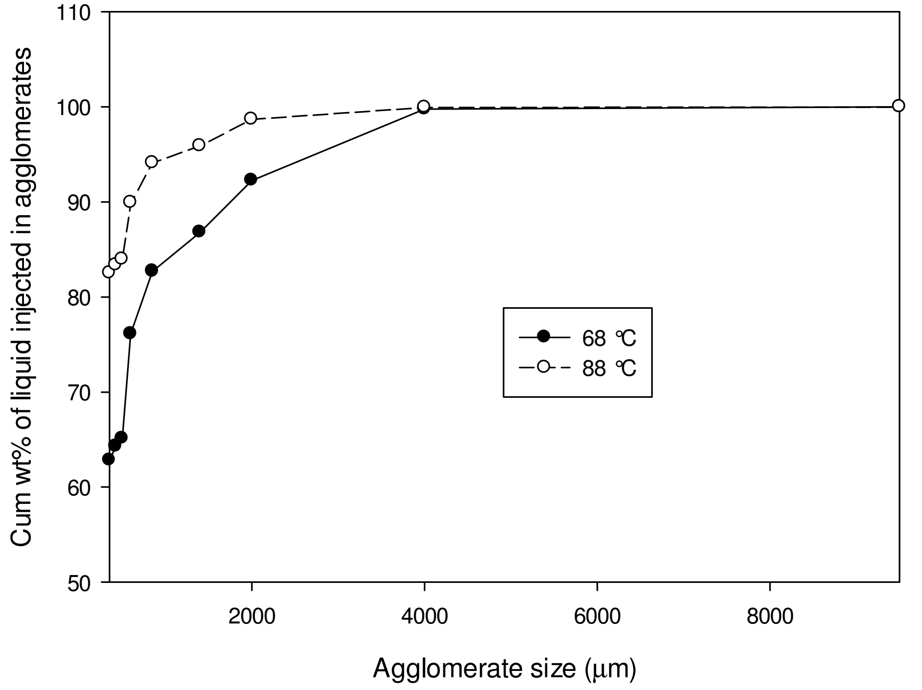

Figure 4-11: Effect of liquid vaporization on liquid distribution

4.4 Conclusions

In the present work, the effect of bed hydrodynamics and vaporization rate of a liquid being injected in a fluidized bed was studied with a model system under conditions relevant to the Fluid Coking^{TM} process. From the results obtained in this study, the following conclusions are made:

- Increasing the fluidization velocity improves the initial liquid distribution and mixing in the jet cavity reducing the quantity of liquid that is trapped in agglomerates;
- Increasing the fluidization velocity enhances the fragmentation of the agglomerates, thus decreasing the total mass of macro-agglomerates formed, while increasing the population of micro-agglomerates;
- The bed temperature has two opposite effects. Because the agglomerates dry faster, they have less opportunity for breakage but, on the other hand, because the initial viscosity of the liquid within the particles is lower, agglomerates formed are weaker and more fragmentation occurs;
- Increasing the bed temperature also improves the liquid distribution by increasing the proportion of the injected liquid that vaporizes within the jet cavity, where it enhances mixing of particles and liquid droplets;
- The results of this study suggest that increasing the fluidization velocity and the bed temperature should improve the liquid distribution in Fluid Cokers^{TM}, although all the implications of such changes on the process should be considered.

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Chapter 5

5 Conclusions and Recommendations

5.1 Conclusions

- A new experimental model for the Fluid Coking^{TM} process has been developed to study liquid feed distribution and agglomerate formation. It has been tested with a pilot plant fluidized bed operating at near room temperature conditions, and with a scaled down version of a typical industrial two-phase spray nozzle. The experimental model uses novel measurement techniques to study the formation of macro- and micro-agglomerates as well as liquid vaporization in a fluidized bed. The new model produces comparable trends to previous models used to mimic liquid-solid interaction in Fluid Cokers, while requiring less energy and providing additional information to study the effect of liquid vaporization on the agglomeration phenomena. It also provides additional flexibility by allowing for the study of the impact of viscosity and wettability on vaporization and agglomeration of properties;

- In agreement with the theory proposed by previous authors on the effect of agglomerate formation on heat and mass transfer processes in Fluid Cokers, experiments conducted with the new model confirmed that agglomerates slow down the evaporation rate of the liquid. Increasing the flowrate of atomization gas in a scaled-down version of a spray nozzle used in the Fluid Coking^{TM} process, enhances liquid distribution and reduces agglomerate formation. As a result, liquid vaporization is less inhibited and higher liquid yields are expected in Fluid Cokers;

- Physical properties of the liquid greatly affect the performance of the spray nozzle used in the Fluid Coking^{TM} process. Decreasing simultaneously the viscosity and wettability of the liquid solution results in 50% fewer agglomerates with lower liquid concentrations;

- The performance of the conventional TEB nozzle design that is currently being used in Fluid Cokers can be enhanced by using specially design nozzle attachments. However, the improvement in nozzle performance relies on the proper selection of the attachment used:
    - A Clover Leaf attachment at the tip of the nozzle, such as the one used in this study, seems to have a minor, detrimental impact on nozzle performance. It increases agglomeration and the amount of liquid trapped in agglomerates;
    - Satellite jets at the periphery of the conventional TEB nozzle (Satellite Nozzle), on the other hand, have a beneficial impact on nozzle performance. This confirms findings from previous authors and suggests that similar improvements could be achieved for the bitumen–coke system. The Satellite jets greatly improve liquid distribution by disturbing the jet boundary and allowing more solids to be entrained into the jet cavity, resulting in the formation of fewer macro-agglomerates and more micro-agglomerates with lower liquid concentrations, which are less of a problem in terms of heat and mass transfer limitations;

- Bed hydrodynamics and operating conditions can have a significant impact on agglomerate formation and liquid distribution. Increasing the fluidization velocity not only enhances agglomerate fragmentation in the fluidized bed, but also improves mixing in the jet cavity due to a higher bubble frequency, resulting in fewer macro-agglomerates with lower liquid concentrations. Increasing the bed temperature has two important effects: it reduces the initial viscosity of liquid trapped in agglomerates resulting in weaker agglomerates that exhibit more fragmentation, and it also increases the vaporization rate of the liquid. The liquid being vaporized in the jet cavity increased the volumetric gas flowrate by 72%, enhancing radial mixing of liquid droplets and entrained particles, resulting in agglomerates with lower liquid concentrations.

5.2 Recommendations

- The results obtained in this study on the agglomerating phenomena and their effects on liquid vaporization should be included in a theoretical model for agglomerate formation in the Fluid Coking^{TM} process. This model would provide more insights on the agglomerating mechanisms and their influence on the bitumen upgrading reactions;

- The use of Satellite Nozzles is expected to improve liquid distribution and reduce agglomerate formation in Fluid Cokers. Experiments are suggested at a larger scale and attention should be given to their mechanical strength and reliability under more severe conditions such as the conditions encountered in industrial Fluid Cokers^{TM};

- The new experimental model developed in this work and the methodology employed to measure liquid vaporization and agglomerate properties in laboratory fluidized beds can be used to incorporate not only a liquid injection section, as in this study, but also a section with attrition nozzles and a stripper section, as in industrial Fluid Cokers^{TM}.

Appendices

Appendix A: Washburn technique for determination of the contact angle

A.1. Description of the Washburn Technique

One way to characterize liquid-solid interactions is by closely examining the spread of the considered liquid on the surface of solid particles. This mechanism is widely known as wettability and can be easily quantified by measuring the angle formed between the liquid droplet and the solid surface at the liquid-to-solid interface. (Figure 1-2). This angle is a function of the balance between the shear and capillary forces acting at the liquid-solid interface[1]. A widely used and relatively accurate technique to measure this parameter is the Washburn technique.

Figure A - 1: Wettability of a solid by the contact angle12

This technique is based on the linear relationship between the square of the length of penetration of the liquid and the time it takes the liquid to travel that distance, given by Equation A.1[2],

$$\frac{l^2}{t} = \frac{D_{tube}}{4}\frac{\gamma}{\eta}cos\theta \qquad (A.1)$$

Where *l* is the penetration length, *t* represents the time for the liquid to penetrate a length *l* of the powder, γ and η are the surface tension and viscosity of the liquid, respectively, and *θ* is the contact angle. By relating the length of penetrated liquid to the wetted mass of the associated solid, Equation A.1 becomes,

$$\frac{M^2}{t} = \frac{\pi^2 {D_{tube}}^5}{64}\frac{\rho_l^2\gamma}{\eta}cos\theta = C_w\frac{\rho_l^2\gamma}{\eta}cos\theta \qquad (A.2)$$

In Equation (A.2), the constant C_w depends only on the geometry of the powder bed. Then, in order to determine the value of C_w for a given powder, a reference measurement must be performed with a liquid that perfectly wets the solid with a 0° contact angle[13].

In this study, the Washburn technique has been used to determine the wettability of a new system proposed to mimic the liquid-solid interactions between bitumen and coke at operating conditions

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- Morales M., C.B., Jamaleddine, T.J., Briens, C., Berruti, F., McMillan, J., "Effect of Liquid Properties and Spray Nozzle Design on Agglomerate Properties in a Fluidized Bed"

- Morales M., C.B., Jamaleddine, T.J., Briens, C., Berruti, F., McMillan, J., “Effect of Bed Hydrodynamics and Liquid Vaporization Rate on Agglomerate Properties in a Fluidized Bed”