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Particle agglomeration in gas-liquid-solid fluidized beds with a dispersed immiscible liquid: Study on particle size, shape and material

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ABSTRACT

The formation of a denser and more viscous secondary liquid phase may impact the fluid dynamic behaviour of industrial ebullated bed reactors such as hydroprocessors. This study investigates the effects of particle size, shape and material on the global fluid dynamic behaviour of gas-liquid-liquid-solid fluidized beds subject to particle agglomeration. Ebullated bed experiments were carried out in a 152.4 mm diameter column at atmospheric conditions with biodiesel as the continuous liquid, 5 wt.% of glycerol as the denser and more viscous dispersed liquid, and nitrogen. Glass spheres with diameters of 4 and 1.5 mm were compared to aluminum cylinders with equivalent volume to surface area ratios, where the sphericity of both larger and smaller cylinders was approximately 0.8. In a liquid-solid fluidized bed, the previous particles were in the intermediate settling flow regime ($0.2 < Re_{LT\infty} < 500$) in biodiesel; nonetheless, coalescing and dispersed bubble flow regimes were obtained with the smaller and larger particles, respectively, at the introduction of gas. Liquid-liquid-solid fluidized bed results established that particle size, shape and material had considerable impacts on agglomeration behaviour. In the gas-liquid-liquid-solid ebullated bed, the 1.5 mm glass beads transitioned from coalesced to dispersed bubble flow due to increased particle inertia from agglomeration. Larger glass beads experienced a reduced bed expansion due to agglomeration since the bubble flow regime remained constant. The studied aluminum cylinders did not agglomerate to the same extent as the glass beads due to differing material wetting properties, where negligible clustering occurred with the larger cylinders and an axial agglomerate size distribution was observed with the smaller cylinders. Preliminary experiments in a slurry bubble column using 100 to 150 μm glass beads were inoperable at a relatively low glycerol concentration of 0.7 wt.% due to considerable sedimentation on the distributor. Interparticle forces relevant to gas-liquid-liquid-solid fluidized beds are discussed, with an emphasis on the relation between fluid and particle properties with respect to attractive forces due to liquid bridging.

1. Introduction

Ebullated bed hydroprocessors operate as gas-liquid-solid fluidized beds to promote contact between the gas (mostly hydrogen), liquid (resid feed and converted fractions) and solid (alumina supported catalyst) phases. Hydroprocessing combines thermal cracking at elevated temperatures (~440 °C) and hydrogenation at elevated operating pressure (~11.7 MPa) to convert the heavier liquid feed material to lighter fractions [1]. LC-Finer^{SM} ebullated bed resid upgraders operate with co-current flow of gas and liquid through a bed of cylindrical heterogeneous catalyst particles sized in the mm range. The catalyst bed is fluidized mainly due to the liquid flow, where an internal liquid recycle line increases the liquid residence time and controls the catalyst bed expansion. Another resid hydroprocessing configuration is the slurry bubble column (e.g., VEBA-combi-cracking, M-coke technology, HDH technology, and UOP Uniflex^{TM}) which uses dispersed unsupported catalysts in the μm range, where catalysts are primarily suspended from local liquid flow induced by the wakes of rising bubbles.

Upgrading heavier feeds can lead to coke formation in hydroprocessors, largely due to accelerated thermal cracking at elevated temperatures, which can cause reactor/downstream equipment fouling and reduced catalytic activity [2]. Coke is generally defined as toluene insoluble materials and is believed to originate from the asphaltene fraction in the feedstock [3]. An intermediate phase between the heavier liquid fraction and solid coke, commonly referred as carbonaceous mesophase, was initially identified by its optical anisotropy when observed under polarized light [4]. Some potential formation mechanisms have been discussed by previous authors [5–8], where the intermediate phase is believed to form due to an increased rate of thermal cracking relative to the rate of hydrogenation. If the cracking rate of alkyl chains from polyaromatics cores increases relative to the rate of aromatic core hydrogenation, resulting planar polyaromatic cores may oligomerize/coalesce to form initial mesophase domains. A recent study by Bagheri et al. [5] observed the in-situ formation of both small and large mesophase domains with areas below and above 2000 μm^2, respectively, in a stirred

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hot-stage reactor at 440 °C and 4.8 MPa. Larger mesophase domains, which resulted from the coalescence of smaller domains, were minimized with the addition of a proprietary catalyst as the particles attached themselves to the mesophase outer surface. Although it is difficult to know whether carbonaceous mesophase is present in industrial ebullated beds and/or its approximate concentration, mounds of agglomerated catalysts and coke have been previously found above the grid during shutdowns [1].

Mesophase may impact the fluidization behaviour of ebullated bed and slurry hydroprocessors, particularly if the additional phase leads to particle clustering. Few studies are currently available in the open literature with regards to the effect of an additional immiscible liquid in ebullated beds and/or slurry bubble columns. Mass transfer parameters in bubble columns with an additional liquid phase have been previously studied [9,10] due to the dispersed liquid's potential to increase gas absorption. Studies on liquid-liquid-solid fluidized beds have investigated dispersed drop properties, pressure fluctuations and interphase mass transfer coefficients mostly for liquid-liquid extractions as the particles can improve the contact between both liquid phases [11–16]. Siquier et al. [17] and Argüelles et al. [18] studied the solid and gas axial holdup profiles in slurry bubble columns, where the continuous and dispersed liquid phases were kerosene and water, respectively.

Particle agglomeration is also relevant to fluid coking, a complementary process for resid upgrading, where the liquid feed is injected in a gas-solid fluidized bed of coke particles. Although different from ebullated beds and slurry bubble columns, agglomeration studies in gas-solid fluidized beds provide an initial comparison for clustering behaviour. The stability of prepared agglomerates, using water as the liquid and glass beads or silica sand as the solid, was investigated in a gas-solid fluidized bed [19] while a subsequent study examined the effects of agglomerate size/density, liquid viscosity, binder concentration and gas velocity [20]. Agglomerates were also examined using coke particles and oil to better represent the industrial particle properties [21]. Artificial agglomerates made of polyurethane foam, magnets and RFID tags were employed to study the stability of spherical [22] and cylindrical shapes [23]. McMillan et al. [24] discuss the cohesive forces between particles in fluidized beds operated in the bubbling and fast fluidization regimes as well as when liquid jets are introduced. They used FCC catalyst, glass beads and sand, where the particle sizes were in the range of 70–220 μm. High speed video and image analysis demonstrated significant particle clustering, particularly due to cohesive bridging when a liquid was injected. Effects of selected liquid properties in a cold-model gas-solid fluidized were studied by Mohagheghi et al. [25], where the liquid viscosity and contact angle had a considerable impact on particle cohesiveness and agglomerate formation.

An initial ebullated bed study investigated the impact of a dispersed immiscible liquid phase on the overall phase holdups and fluidization behaviour in a cold-flow non-simulating system using biodiesel as the continuous liquid phase, glycerol as the dispersed liquid phase, 1.3 mm diameter glass beads, and nitrogen [26]. It is important to note that the previous experimental conditions were not representative of the industrially observed high gas holdup conditions in ebullated bed hydroprocessors [1]. Bubble column experiments demonstrated that added glycerol reduced the gas holdups, where dynamic gas disengagement profiles revealed an increased large bubble population and reductions to the small and micro bubble holdups. Conversely, glycerol addition changed the bubble characteristics and fluidization behaviour in the ebullated bed from coalescing to dispersed bubble flow due to an increased apparent particle size via agglomeration.

The purpose of this study is to expand on the previous study by qualitatively and quantitatively investigating the impact of particle size, shape and material on agglomeration tendencies in an ebullated bed using two sets of spheres and cylinders with equivalent Sauter mean diameters. Liquid-liquid-solid fluidized bed results are used as an initial indicator of agglomeration tendencies and to estimate the change in cluster size due to increased liquid flow. Ebullated bed results study the impact of gas and liquid flow rates on the fluidization behaviour with particle agglomeration. Preliminary experiments in a slurry bubble column further demonstrate the impact of particle size relative to particle clustering. As the measurements are carried out in a non-simulating system, the experimental results thus provide fluid dynamic trends following particle agglomeration in gas-liquid-solid fluidized beds. Lastly, the discussion focuses on interparticle forces, particularly liquid bridging, which can lead to agglomeration in gas-liquid-liquid-solid fluidized beds.

2. Materials and methods

2.1. Experimental system

Experiments were performed at ambient temperature and pressure in a clear polyvinyl chloride column with a maximum expanded bed height of 2.7 m and an inner diameter of 0.1524 m, adequately large to minimize wall effects on phase holdups [27]. A schematic of the experimental setup is provided in Fig. 1. The gas and liquid were separately introduced to the bottom of the fluidized bed to facilitate uniform spatial distribution of the fluids. The gas-liquid distributor was a perforated plate with 62 holes of 4.0 mm diameter for liquid flow, while gas was introduced via 32 holes of 0.8 mm diameter. A mesh placed on top of the distributor was used to prevent particles from entering the

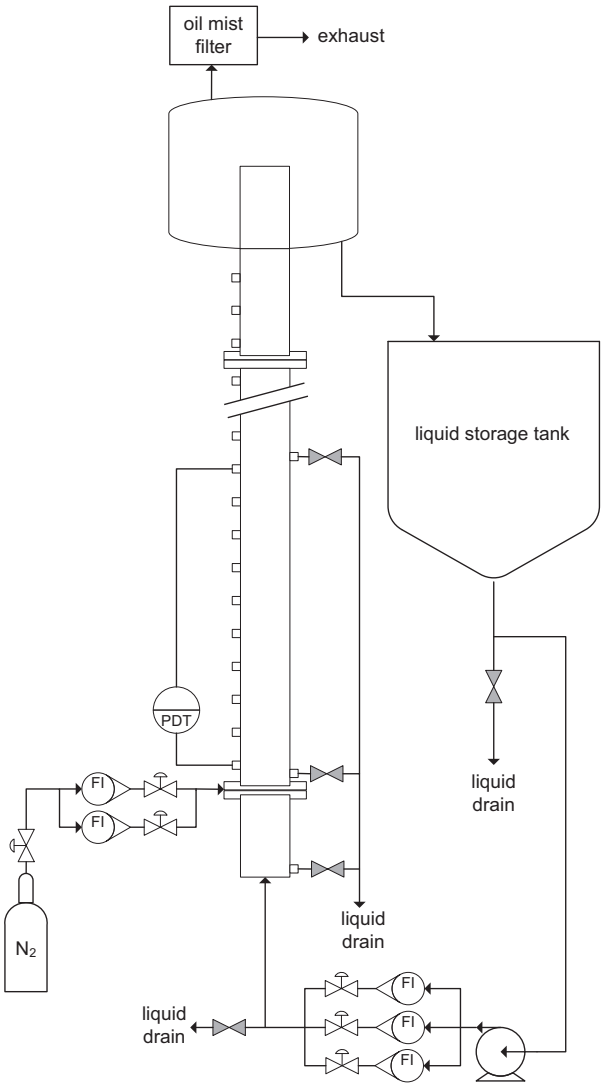

Fig. 1. Schematic of the fluidization column for organic liquids.