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Filtration and Catalytic Reaction in Trickle Beds – Use of Solid Foam Guard Beds to Mitigate Fines Plugging

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Résumé

La sensibilité des réactions catalytiques à la filtration et le dépôt simultané de fines dans les réacteurs à lit ruisselant ont été évaluées au moyen de l'hydrogénation catalytique de l' α -méthylstyrène présent dans des suspensions diluées de kaolin dans du kérosène. Nous avons observé une corrélation négative entre la conversion catalytique et l'ampleur du dépôt spécifique au sein du lit engendrant une étape supplémentaire de transfert de masse au travers du dépôt en croissance sur les collecteurs. La sévérité de la résistance au transfert de masse est sensible à la compaction du dépôts autour des collecteurs qui est influencée par l'importance des vitesses superficielles de gaz. En outre, les pertes irréversibles observées concernant l'activité du catalyseur ont été attribuées, après avoir débarrassé le catalyseur de son dépôt, à une perte de sites actifs par le piégeage de fines dans les microporosités du catalyseur. L'accumulation de fines dans le lit de catalyseur a été notablement réduite par l'adjonction en amont du lit de modules à base de mousses inorganiques (d'alumine ou de carbure de silicium) à haute porosité et faisant office de filtres de garde. Des études hydrodynamiques ont été réalisées avec et sans les blocs de mousse pour évaluer leur rôle sur la répartition de la suspension, la réduction du dépôt spécifique et la chute de pression dans le lit ruisselant. Il a été constaté que l'efficacité de capture par les blocs de mousse dépend de la connectivité et du degré d'ouverture des cellules dans les mousses ainsi que de la nature physico-chimique des matériaux constitutifs. Le nombre de modules de mousse a affecté la réduction des dépôts spécifiques et la chute de pression dans le lit. Ceci indique une possibilité de prolonger la durée de vie des réacteurs d'hydrotraitement à lit ruisselant à l'aide de lits de garde à base de mousse.

Abstract

The sensitivity of catalytic reactions to concurrent filtration and fines deposition in trickle bed reactors was assessed by means of the catalytic hydrogenation of α -methylstyrene from kaolin-kerosene suspensions flows. A negative correlation between catalytic conversion and bed specific deposit resulted from the extra-mass transfer step that built up on the collectors in the course of filtration. The severity of the evolving extra-mass transfer step was sensitive to deposit compaction resulting from higher gas superficial velocities. Furthermore, irreversible catalyst activity losses were observed, after catalyst clean-up, and ascribed to irretrievable active sites by catalyst intra-particle fines trapping. Fines accumulation in the catalyst bed was notably reduced by means of high-porosity solid-foam modules used as guard filters and placed upstream of, and adjacent to, the trickle bed. Hydrodynamic studies were carried out with alumina and silicon carbide solid foams to assess their role on the distribution of suspension and the reduction of specific deposit and pressure drop in trickle beds. It was found that the foam capture efficiency critically depended on the open connectivity of foam cells and the physicochemical nature of foam materials. The numbering up of foam modules led to reduced overall bed specific deposits and pressure drops foreseeing a prospect for prolonging hydrotreating trickle bed reactor life time using solid foam as guard beds.

Foreword

A manuscript prepared from this research study was published in Journal of Industrial & Engineering Chemistry Research (I&ECR. 2012, 41, 1729-1740).

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One chapter is prepared from the article in its integrity. The size of the figures and tables and the size of characters inside of the figures were adjusted to fit with current manuscript format.

Prof. Faiçal Larachi is my research director in this research study.

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*I dedicate this research to my
parents.*

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Chapter 1: Introduction and Objectives

I.1 Oil sands

Oil sands are a mixture of thick bitumen, sand, clays, water and other minerals. The grain of oil sand is surrounded by water and bitumen, forming an outer layer. Crude oils are considerably heavy, but in comparison, bitumen is a lot heavier. Oil sands go by other terms such as, tar and/or bituminous sands. Although oil sands are given the name tar, it is in actuality an inaccurate use of term to describe bituminous deposits. Tar is a substance produced by distilling organic matter. Bitumen is a naturally occurring substance that only has the appeal of tar (Oil Sands Intelligence & Technology).

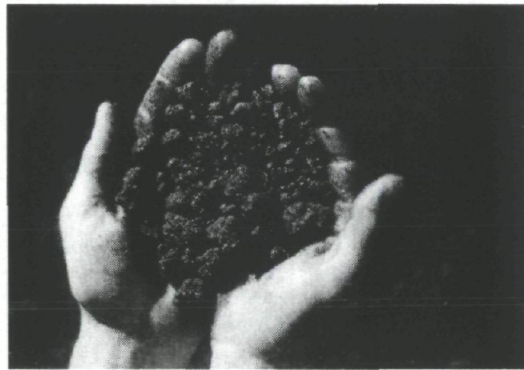


Figure I1 Oil sands

There is growing concern over depletion of conventional oil reserves because of excessive demand which makes Canada's oil sands as part of solution to declining conventional oil reserves elsewhere in the world. According to Canada National Energy Board studies in 2004, Canada has around 2.5 trillion barrels of bitumen (heavy oil) recoverable with present day technology which makes it one of the biggest reservoirs of oil, second only to Saudi Arabia and for over 200 years 2.5 million barrels oil could be produced per day. Presence of such big reservoirs increases importance of oil sands as it is enough to fulfill the demands of not just Canada but also countries like America, China and other oil importers for generations to come.

Oil sands exploration involves methods that are either conventional or unconventional, such as mining and "in-situ" procedures. Bitumen-rich sands are excavated by mining oil sand areas through the procedure of open pit mining. This process is the most suitable and efficient for extracting bitumen when there are large deposits with little overburden. In-situ includes method of processing deposits of oil sands, allowing the bitumen to be separated from the sand itself. These methods are used when it is

not economically feasible to do surface mining in order to extract the bitumen because of their depth underneath the surface. In Northern Alberta, around 80%, of these resources exist deep underneath the surface.

I.2 Bitumen

As stated earlier, Bitumen is highly viscous crude oil. It is sticky and black in color. Bitumen is so thick that it would be unable to flow. The only way for this organic substance to flow is if heated and through dilution with hydrocarbons. It cannot be recovered by pumping from a well in its natural state by using in-situ method. In the mining method, as soon as these oil sands have been excavated, bitumen deposits are then extracted and separated from the sands. This is completed through a process consisting of “four” steps which include, conditioning separation, secondary separation and froth treatment. Companies involved in oil sands use these methods somewhat differently. Syncrude is a company that uses one-stage separations and solvent called toluene, for froth treatment. Another company, Albion Sands uses separation in three stages. They utilize naphtha as a solvent. Naphtha is a colorless and volatile product of crude oil. In order for Bitumen to be refined into everyday petroleum products, such as kerosene and gasoline, it must be upgraded into “synthetic” crude oil.

I.3 Bitumen Extraction Methods

Currently two main types of oil sands exploitation are applied based on the proximity to the ground surface: 1) Mining-based recovery which is applicable for bitumen deposits close to surface (shallower than 75 m) and 2) In-situ extraction methods which are employed for underground deep reservoirs (Alberta chamber of resources, 2004;Czarnecki et al., 2005).

In the oil sands industry, there exist five in-situ extraction methods for bitumen recovery. These include: SAGD, VAPEX, THAI, CSS and Cold Flow. SAGD and CSS are methods most commonly utilized in these industries. VAPEX, THAI and Cold Flow are processes that are still fairly new in these industries and still under experimentation. The product which is obtained after upgrading, called crude oil is created from bitumen. This process is sequential to bitumen recovery.

Cyclic Steam Stimulation (CSS) in this method, Steam has been injected in the well in cycles and then after soaking, oil production starts. First steam is injected inside well at high temperature (300°C) for longer period of time and then well is allowed to settle down for several days to let heat enter oil sands. The hot bitumen is then pumped out of the well, which may take weeks. Injection of steam cycles depends on production rate, if it falls then more steam is injected and after soaking, production is carried out and it goes on until the cost of injecting steam exceeds production costs. In this method

though recovery factor is high which is around 20 to 25 % but the cost of injecting the steam is high. Imperial Oil Company first time used this method commercially in 1985 at cold lake and also being used at Shell Canada's Peace River project.

Steam Assisted Gravity Drainage (SAGD) this method involves two wells, which are drilled horizontally with one at the bottom of the formation and another 5 meters above it. Steam is injected through upper well into the reservoir which melts the bitumen in well and allow it to flow to lower well assisted by gravity and then pumped to surface. SAGD is cheaper than CSS with high production rate of oil, recovery rate of oil is up to 60%. The method is more efficient in the case of high permeability reservoirs, resulting in the lower injection pressures and lower steam to oil ratios (Alberta chamber of resources,2004; Deutsch et al,2005).Some of the projects where SAGD is used are Suncor's Firebag project, Petro-Canada's MacKay River project, and Encana's Foster Creek project.

The Vapor Extraction Process (VAPEX) this method works same as SAGD, but instead of steam hydrocarbon solvents are injected into the upper well which makes the bitumen dilute and allow it to flow. It is much more energy efficient than steam injection and some partial upgrading of the bitumen to crude oil occurs right inside well but it is more expensive than the above mentioned methods even though oil companies are experimenting with it because of its energy efficiency.

In some fields these above mentioned methods are combined to extract the bitumen for example some wells use CSS cycle to condition the bitumen before using SAGD method is applied for production of oil and in some cases oil companies are also combining now VAPEX and SAGD which helps to improve the rates of recovery and save cost of energy.

Toe to Heel Air Injection (THAI) is a relatively new method of extracting heavy oil defining a crucial and significant advantage over previous methods. By combining a vertical air injection well with horizontal production well, bitumen is placed around the toe of the horizontal well and it is heated with steam. Through an approximate three month heating cycle in the bitumen reservoir, the steam is then shut off and air is injected into the vertical well that induces a combustion reaction within the reservoir. Via the controlled injection of air, an approximate 2 metre thick combustion front starts to move along the horizontal well, approximately 10 inches a day toward the heel of the horizontal well. Due to the increase in heat, the bitumen drains into the horizontal production well and under the influence of nature pressure it appears to surface. Due to the combustion the bitumen is heated up to 400 degrees, which partially upgraded the underground oil. The heat in turn causes a portion of the asphaltine content of the oil to be left behind as coke that is in turn source of continued combustion. This method has increased the rate of production by significantly limiting the environmental footprint. In this

process, steaming is done initially with some water which is returned to surface and after treatment returns back to the environment. The method is attributed to Malcolm Greaves of the University of Bath. After extensive testing at Petrobank's Whitesands pilot project south of Fort McMurray, it was positively proven and Petrobank patented the technology, it is now widely anticipated for the preparation of commercial use in other oil sands and heavy oil reserves in western Canada and around the world.

Cold Flow is a production process where bitumen is pumped without the use of heat with help of specialized progressive cavity pumps. The limitation of this method is that it is only implemented in those areas where the bitumen is fluid enough to pump. It is commonly used in Venezuela, in parts of the Athabasca–Wabasca and Cold Lake regions. Recovery rate is low in this method i-e around 5-6 % though it is considered the cheapest method to recover bitumen. Canadian oil companies discovered that removing the sand filters from the wells can increase the production rate though it will increase the production rate of sand with oil. This technique became known as Cold Heavy Oil Production with Sand (CHOPS). Research showed that pumping out large quantities of sand opened wormholes in the sand formation therefore allowing more oil to reach the borehole. Wormholes are permeable sand tubes with an extreme high porosity which extend out of the borehole. The advantage of this technique is better production rates with recovery rate up to 10%. Disposing of large quantity of sand produced during the recovery of bitumen is one disadvantage of this method. The sand was initially spread on rural roads but the government raised concerns of the density of the roads. In more recent years the sand is stored in underground salt caverns.

In each of the above methods, the bitumen that is pumped to the surface is in the form of a bitumen-rich froth. Separation of Bitumen from mined oil sand in the form of froth is performed by using hot water (Clark and Pasternak, 1932). The froth is treated by diluting with naphtha and processing through centrifuges stages to minimize water and solids. The produced bitumen is very viscous (more than 10000 mPa.s) and its density is around 1000 kg/m³. Typically (on mass basis), it contains 85.5 % carbon, 11% hydrogen, 4.7% sulfur and 0.4% nitrogen (Chung et al., 1997).

I.4 Upgrading of Bitumen

Once bitumen is recovered by using either of above mentioned methods it is then passing through upgrading process to get valuable product called synthetic crude oil made from bitumen. The upgrading is carried out in two steps. Bitumen is converted to lighter material in a coker during primary upgrading. The impurities and contaminants such as metals and minerals are removed. First upgrading step improves the quality of raw material but still contains high quantity of nitrogen, sulphur and

unsaturated compounds. The secondary upgrading is performed at high pressure (10 MPa) and temperature (350 to 400 °C) in hydrotreaters to remove impurities like sulphur. Application of TBRs as hydrotreaters in upgrading of bitumen and unconventional heavy crude oil is highly important.

I.4.1 Trickle Bed Reactors

Trickle bed reactor (TBR) is the most common fixed bed reactor in industrial applications. In trickle bed reactor gas and liquid phases flow concurrently downward as shown in Fig I2. Trickle bed reactor is used in various processes i.e. petrochemical and chemical industries, waste treatment, biochemical and electrochemical processes. In plants for effluent treatment, wastewaters streams are treated by trickling filters to remove organic matters by aerobic bacterial actions. In this process, biological growths are permitted to attach themselves to a bed of stone or other support over which the wastewater is allowed to trickle in contact with air. Trickle-bed reactors (TBR) are used extensively for hydrotreating and hydrodesulfurization applications in the refining industry, and hydrogenation, oxidation and hydrodenitrogenation applications in the chemical, biochemical and waste treatment industries (Al-Dahhan et al., 1997).

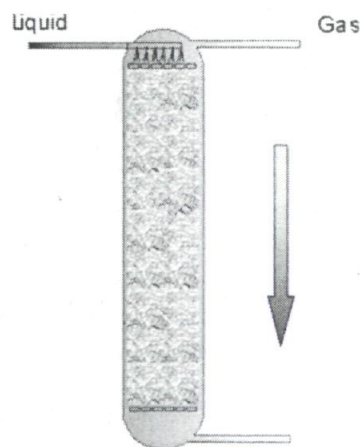


Figure I2 Schematic diagram of trickle bed reactor

In trickle bed reactors a combination of reactions occurs simultaneously during treatment of bitumen i- Hydrodesulfurization(HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), hydrogenation of aromatics and thermal cracking. The reactor consists of catalyst beds 3 m in diameter and up to 10 m high arranged in baskets ca. 2 m high to accommodate that catalyst physical strength. Liquid is redistributed between each bed. Fine particles with different origins exist in the oil stream. They occur naturally in the form of reservoir-mud minerals solids (Naryan et al., 1997). They represent clay

intruders that worm into the mineral processing upstream units. They also originate as coke fines in the cokers through thermally-triggered asphaltene/resin condensation/polymerization of aromatic rings (Wang et al., 1999, 2001; Tanabe and Gray, 1997) or they may be corrosion-induced in upstream equipment such as iron sulphide scales (Tanabe and Gray, 1997; Brossard, 1996).

1.4.2 Problem being Faced by Current Industry

During hydrotreating of bitumen some of the fine particles could enter hydrotreaters and their presence could impede the hydrotreating reactions from going smoothly and after some period of time because of deposition of these fine particles on the surface of catalyst one expects plugging to arise, most likely via depth filtration mechanisms. During hydrotreating process, fine particles with size less than 20 μm can manage to pass through the upstream filters, who can remove particles efficiently greater than 20 μm and these particles penetrate inside trickle bed reactor. Although the concentration of these particles is so low, significant amounts of them can accumulate in the bed due to processing hundreds of barrels per day. This accumulation of fine particles over the surface of catalytic bed cause extra resistance against two-phase flow which ultimately increases pressure drop in the reactor which could finally be excessively high so that operation has to be shut down before the activity of the hydrotreating catalyst is fully used (Gray et al., 2002). The unscheduled shutdowns are time and money consuming equivalent to profit loss.

1.4.3 Trickle Bed Plugging and Depth Filtration

By the time as early as 200 BC, there has been evidence for the use of granular beds for water treatment (Tien and Ramarao, 2007). Granular beds are filled with collector, roughly 0.6 to 2 mm in diameter and filled up to 1 m in height. The mechanism of filtration in granular beds has undergone through many studies in order that it may be understood. In trickle bed reactors, the size of the catalyst pellets range from about 1 to 3 mm and its packing could be up to as high as 10 m. The phenomenon of filtration is very complex due to the presence of the gas phase in the bed but the same mechanisms as that of granular beds are considered to exist during collection of fine particles (Ortiz and Larachi, 2005). According to Tien and Ramarao (2007), a two step process can be considered for the deposition of particles from suspension as it flows over the collector. The first process involves the transporting of particles from suspension to the vicinity of a surface and second step involves its adhesion to the surface. This adhesion to surface depends only on the nature of interaction of a surface to particle. A particles bonding or lack of bonding depends on a net result involving short forces. Such forces include the London-van der Waals (dipole moments around nuclei) and double layer interactions (electrical) that arise because of charges in the surface. These surface charges are gained by solid material in a

liquid through different types of mechanisms. Surface charges are in balance by “counter” charges found in the liquid. This establishes a double layer of charge that is characterized by a potential difference between two objects, a material surface and a solution called zeta potential. Repulsive double layer force between particles and the collector of the same electrical charge can be so strong to prevent the deposition (Chowdhia, 1981). These particles are transported to a collector surface by mechanisms called sedimentation, inertial impactions interceptions, straining and Brownian diffusion.

When particles follow the same path as the fluid, they experienced inertial impaction. In the collector’s proximity, the path of fluid (streamlines) changes its direction in order for it to conform to a no slip situation when it is at the collector surface. Particles change their position and/or aim (trajectory) differently due to inertia. Some of the particles intersect with the collector surface while others may separate from the streamline. This type of mechanism is important when it comes to gas filtration. In gas filtration, particles gain a significant amount of inertia because of a fluid having high velocity. Particles are able to be captured through a process called interception. The reason for this is because these particles are finite in size and the particles which come within one particle’s radius from the collector surface could be assumed to be captured. When the density of the particle is greater than the fluid itself, they will settle in the direction of the force of gravity. Brownian diffusion is considered significant for any submicron particles. When the size of the particle in a suspension is greater than the constriction of pores, through which this suspension will flow, these particles would be retained. This mechanism is called straining or sieving. Deposition through straining will lead to formation of filter cake at a bed inlet which ultimately will increase the pressure drop suddenly and significantly to maintain a constant flow across the bed.

Gray et al. (2002) studied the phenomena of filtration in trickle bed reactor while using air and kaolin-kerosene suspension as test fluids, operating under trickle and pulse flow regimes during two phase flow. Kaolin-kerosene suspension was prepared and re-circulated to the reactor and occasionally kaolin was added as a makeup in suspension. Experimental results showed that pressure drop increased with passage of time monotonically with concentration of clay fines in bed and results showed that clay was distributed along the packed bed relatively uniformly in both flow regimes.

Wang et al. (1999, 2001) investigated that hydrogenation reaction environment could influence the rate of filtration of fine particles due to change in chemistry of surface. Surface of kaolin particles were modified by adsorption of polymeric asphaltene molecules. This change in surface chemistry results in change of mechanism of filtration from cake filtration to deep bed filtration. It reveals that extent of filtration decreases with overall increase in concentration of adsorbed asphaltene on surface of kaolin.

Iron sulphide is produced due to the affect of hydrogen sulphide on the corrosion products in hydrodesulfurization. Results showed that asphaltene-coated kaolin is deposited less readily than asphaltene-coated iron sulphide at hydrotreater conditions, because the mineral surface did not retain a stabilizing layer of asphaltenic material.

Iliuta and Larachi (2005 a, b) studied the impact of periodic flow on filtration in trickle bed reactor in order to diminish the deposition of fine particles on surface of catalyst. The model was proposed for the two phase flow space evolution of both deposition and detachment of fine particles in trickle bed reactors and that model was based on the volume average mass and momentum balance equations and volume average continuity equation for fine particles. The specific deposit and pressure drop were calculated. The results show that specific deposit reduces with periodic operation for non-Brownian particles. The release of fines was more intense for larger particles than smaller ones. This technique is not a proper solution for Brownian particles as they possess high critical shear stress which makes its non-applicable.

Edouard et al. (2006) investigated the effect of gas superficial velocity on dynamics of plugging phenomena in trickle bed reactor. Air and kerosene/kaolin were selected as test fluids during experiments. The suspension was circulated and kaolin makeup was added to the reservoir during the experiment. Their results showed decline in specific deposit with respect to change in gas superficial velocities from low to moderate. It was found that filter coefficient is sensitive to liquid holdup and specific deposit and an empirical relationship between filtration rate and the liquid holdup in trickle beds was established.

M.Hamidipour et al.(2007) studied the hydrodynamics of trickle bed reactor with filtration under cyclic operation to investigate the effect of periodic flows over reduction of deposition of fine particles on surface of catalyst and hence to extend the reactor operational life. Air and suspension of kaolin/kerosene were selected as test fluids and studies were done to have deep understanding of liquid-gas and alternating liquid-gas cyclic operations during single-pass two phase in trickle bed reactor. Results show that fast- and slow-mode liquid cyclic operation policies had no influence on pressure and specific deposit i-e couldn't decrease it while using this strategy; however, with careful adjustment of parameters of liquid cyclic operation it would be possible to prolong the trickle-bed cycle life. Alternating gas-liquid cyclic feed was also proven a useful strategy to reduce the pressure drop and specific deposit of bed with same efficiency for both short and tall beds.

M. Hamidipour et al. (2007b) investigated the effect of filtration of micrometer scaled fine particles, contained in the flowing suspension, on the various hydrodynamic parameters of trickle bed reactor

which includes the filtration efficiency, two-phase pressure drop, and bed specific deposit (mass of deposited fines per unit of reactor volume). These were monitored in the air-kerosene-kaolin particles system to study the effect of packing (smooth and porous collectors), bed height, distribution of suspension at the bed entrance, addition of makeup in recirculation mode, gas superficial velocity, and flow regime transition. A seamless pattern was not observed during development of deposition, there was formation of scattered mesoscale islands of deposits where were separated by plug-free large multiple interconnected pores. These scattered mesoscale islands cause maldistribution in bed that favoured short-circuiting of the flow and levelling off of the bed pressure drop. A non-systematic transition from trickle flow to pulse flow was observed due to increase in bed obstruction with passage of time, and to occur, it required a minimum clean-bed starting liquid holdup value.

M.Hamidipour et al. (2009) studied development of deposition with the help of Electrical Capacitance Tomography imaging (ECT) technique in trickle bed reactor. Hydrocarbon liquid used during filtration experiments was nonpolar oil-like suspension. The ability of ECT to measure accurately was validated in the pristine (deposit free) bed state by doing the comparison between liquid holdup measurement from ECT and liquid holdup measurement from residence time distribution (RTD) method. Parameters studied during filtration experiments were, the effects of the initial liquid suspension distribution, the gas and liquid superficial velocities, and single-phase flow (i.e., zero gas velocity) on the structure of the deposition in the bed. ECT imaging successfully tracked the unsteady-state progression of bed plugging throughout the trickle bed. Results show that local deposition increased with increase in gas or liquid superficial velocity. ECT was also used to determine the transition from trickle flow to pulse due to the deposition of fine particles inside bed and formation of filter cake was observed on top of bed in absence of gas.

1.5 Foam Packing

Solid foam matrices have been recently introduced and present a highly permeable porous structure with a high porosity (0.60–0.95), which enables a considerable reduction of the pressure drops along the catalyst bed even at high gaseous space velocity with a high specific surface area and on the other hand, the solid ligaments (or struts) in foam material allows the continuous connection of the different catalyst domains which increase the effective thermal conductivity on the entire system without thermal breaking points as encountered with the packed bed. Different kinds of materials have been used to produce these solid foams with different geometries and shapes (metal, ceramics, carbon, SiC and polymers) as shown in Fig. The use of porous structures with high external surface area represents an important breakthrough in industrial catalytic applications. The main advantage of using these

porous structures is the high contact surface between the fluid and solid phase and also the low pressure drop along the catalyst bed. During the last decade there has been a growing interest in catalytic reactor engineering based on structured catalytic beds (G. Groppi, E. Tronconi, 2007 , L. Giani, G. Groppi, et al., 2005). The idea of moving from the traditional packed-bed, e.g. extrudates, pellets, to the structured bed, i.e. monolith, wire or foam either made of stainless steel or ceramic, is become more and more popular, packed bed induces an important pressure drop at high flow which is detrimental for the operating system, especially when high space velocity is required for maintaining acceptable selectivity by phasing-out the unwanted secondary reactions.

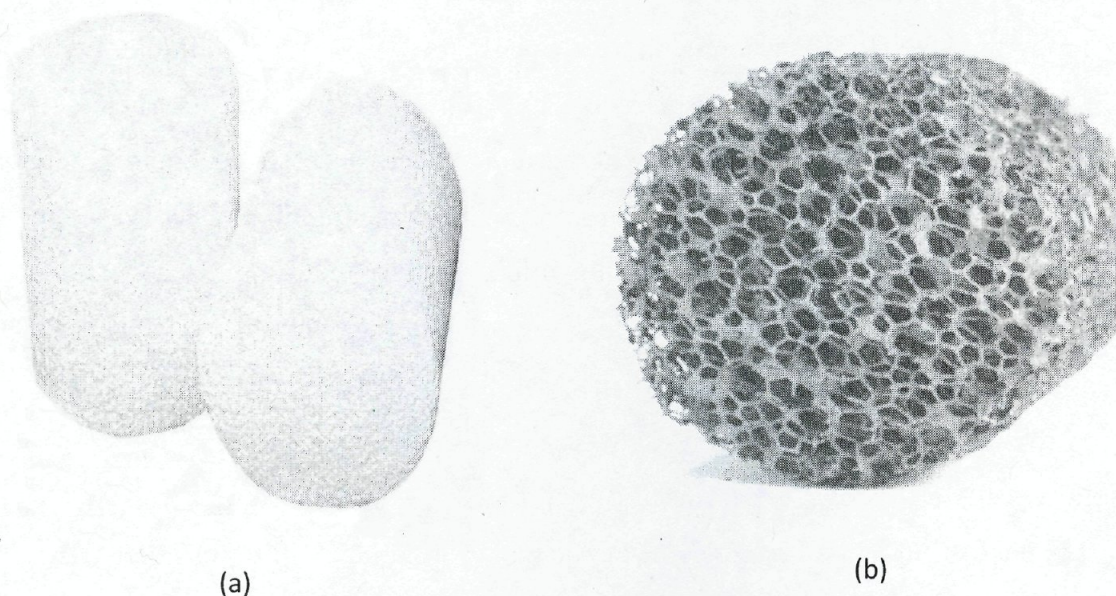


Figure 13 (a) Alumina Foams (b) SiC Foam

Objective

Trickle Bed reactors have great importance in process industry and while processing the fluids polluted with small particles in petroleum-like conditions can impose drastic operating problems. The research studies have been done to account the plugging phenomena but no such literature or study is found on effect of this plugging because of deposition of fine particles on catalytic conversion reaction while processing the fluids. The necessity of research to understand the relationship between deposition of fine particles on surface of catalyst and chemical conversion reaction is truly felt. Experiments were carried out to investigate the effect of deposition of these fine particles present in fluid on surface of catalyst on chemical Reaction. The solution strategy to mitigate the deposition of these fine particles present inside fluid could include usage of foam modules as upstream guard in trickle bed reactor to capture the fine particles present inside fluid and keep the catalytic bed as clean as possible which ultimately could improve the conversion and prolong the life of bed.

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Chapter 2: Filtration and Catalytic Reaction in Trickle Beds – Use of Solid Foam Guard Beds to Mitigate Fines Plugging

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Abstract:

The sensitivity of catalytic reactions to concurrent filtration and fines deposition in trickle bed reactors was assessed by means of the catalytic hydrogenation of α -methylstyrene from kaolin-kerosene suspensions flows. A negative correlation between catalytic conversion and bed specific deposit resulted from the extra-mass transfer step that built up on the collectors in the course of filtration. The severity of the evolving extra-mass transfer step was sensitive to deposit compaction resulting from higher gas superficial velocities. Furthermore, irreversible catalyst activity losses were observed, after catalyst clean-up, and ascribed to irretrievable active sites by catalyst intra-particle fines trapping. Fines accumulation in the catalyst bed was notably reduced by means of high-porosity solid-foam modules used as guard filters and placed upstream of, and adjacent to, the trickle bed. Hydrodynamic studies were carried out with alumina and silicon carbide solid foams to assess their role on the distribution of suspension and the reduction of specific deposit and pressure drop in trickle beds. It was found that the foam capture efficiency critically depended on the open connectivity of foam cells and the physicochemical nature of foam materials. The numbering up of foam modules led to reduced overall bed specific deposits and pressure drops foreseeing a prospect for prolonging hydrotreating trickle bed reactor life time using solid foam as guard beds.

Keywords Trickle bed; filtration; hydrogenation; hydrodynamics; deposition; pressure drop; electrical capacitance tomography; solid foams.

1.1 Introduction

Trickle bed reactors (TBR) are randomly packed beds of catalyst particles in which liquid and gas phases flow concurrently downwards. They are widely used for heterogeneous catalyzed reactions especially hydrogenation reactions in oil refining, petrochemical, and chemical industries. Application of TBRs in upgrading of bitumen and unconventional heavy crude oil is highly important. Unconventional heavy crude oil and bitumen are nowadays increasing their commercial penetration with respect to conventional crude oil resources.¹ Uplifted by a respiteless global demand and harbingers of a looming global oil peak, current high-oil prices are invigorating the stature of Canadian oil sands which are increasingly contemplated as substitutes to conventional crude oil.²

Oil sand is a naturally occurring mixture of water, minerals and bitumen, which is heavy and extremely viscous oil. The crude oil contains a mixture of hydrocarbon compounds and relatively high quantities of other materials such as oxygen, nitrogen and sulfur. The removal of sulfur-containing compounds from streams comprising such compounds has always been of considerable importance in the past and is even more now in view of continuously tightening environmental regulations. The sulfur contents are removed by hydrogenation reaction in TBRs, with a co-current down-flow hydrogen rich gas stream and a liquid hydrocarbon feed. The hydrocarbon stream contains fines comprised of silt, very fine quartz and clay minerals. These fine particles along with coke particles from upstream delayed cokers and corrosion products with size less than 20 μm pass through all the upstream filters and carry over in the heavy gasoil fractions to hydrotreaters.

The presence of fines in the liquid stream might impede the hydrotreating reactions from going smoothly, and in the long-term, because of deposition of some fines on the catalyst surface one expects plugging to arise, most likely via depth filtration mechanisms. Two-phase pressure drop along the bed will increase progressively with time.³ Current industry practice allows for collecting fine particles during the hydrotreating process. The bed collects fine particles until the pressure drop reaches a critical limit which then forces reactor shutdown. This rise in pressure drop is not desirable because it leads to overexploitation of recycling compressors and hydrogen partial pressure at reactor outlet is crumpled. Build-up of fine deposition not just increases pressure drop, it also blocks the physically active catalyst sites ultimately causing loss in reactor catalytic performance. Catalyst replacement is often required well before the catalyst activity is exhausted, occasioning additional costs and a loss in process competitiveness.⁴

Hydrodynamic studies have been done on plugging phenomena and two-phase pressure drop³⁻⁸ and different techniques have been proposed to reduce deposition of these fine particles. Monolith configuration was tested to find out whether straight channels could reduce the extent of deposition. Performances of 1-mm channel monolith and trickle bed reactors were compared. Less pressure drop with 50% less deposition for similar collector area and operating conditions was noticed with monolith reactors.⁶ Flow modulation strategies have also been tested to reduce deposition in TBRs. These can reduce the amount of deposits by detaching, re-entraining and clearing deposits owing to the imposed waves.⁹ Injection of electrical conductivity improvers (ECI) during filtration was also investigated to prompt surface charge changes.¹⁰ As collector charge remain unaltered, repulsive forces between surfaces charged alike will cause removal of the deposits. A theoretical analysis of the deposition of fine particles under chemical reacting conditions in TBRs was performed¹¹ using a dynamic multiphase flow deep-bed filtration model coupled with reaction, heat and species balance equations in the liquid, gas and solid (catalyst + deposit) phases. The simulations indicated that deposition did influence appreciably reactor performance and the only undesirable effect of fines deposition was bed plugging and increase of the resistance to two-phase flow. However effect of deposition of fine particles on catalyst surface on catalytic conversion in TBRs is still currently un-investigated. Thus no substantial literature is yet available to assist in understanding fully the relationship between deposition of these fine particles on the surface of the catalyst and catalytic conversion in TBR during filtration.

Foam structures have been recently introduced to overcome some of the drawbacks packed bed has been facing. Their porosity is high with respect to packed bed which enables considerable reduction of pressure drop per unit length even at high space velocity.¹²⁻¹⁴ This is mainly due to the open-celled structures with relatively high voidages. Foam structures besides having high porosity also give high external surface area and high contact surface between the fluid and solid phase which can enhance mass and heat transfers.¹⁵ They were also shown to exhibit in two-phase operation pressure drops that are much lower and liquid holdup much larger than in conventional trickle bed reactors for the same operating conditions.^{16,17} Different kinds of materials have been used to produce these solid foams with different geometries and shapes (metal, ceramics, carbon, SiC and polymers). Different methods and techniques have been exposed in the literature to produce solid foams.¹⁸

The aim of the present work is to investigate the loss in reactor performance and activity due to deposition of fine particles and to propose a new method to reduce fines deposition in catalytically active beds. For this purpose, two different types of foams, alumina (Al_2O_3) and silicon carbide (SiC), were selected. The foams were utilized as upstream guards to capture fines and to monitor whether they

could help reducing deposition of fines on the surface of catalyst during filtration. This is expected to lead to less pressure drop and prolonging the life of the catalytic bed. A further advantage of using these foams is that instead of replacing the whole catalytic bed, it is easier to clean these foams and they could thus be reused as upstream guards. Electrical capacitance tomography (ECT) is used to monitor inception and evolution of deposition during the hydrodynamic studies. The chemical reaction study in this investigation concerns hydrogenation of α -methylstyrene to cumene. It was selected because it proceeds with an appreciable rate even at low temperature and low hydrogen solubility (at atmospheric pressure), it is (gas-limited) mass-transfer controlled and cumene is the only measurable product.

1.2 Experimental Setup and Methods

To study the effect of fines deposition on reaction conversion, catalytic hydrogenation experiments were carried out in two steps. Fines deposits were first built up on the surface of catalysts (i.e., deposition sequence) and then a catalytic reaction step was resumed (i.e., reaction sequence).

1.2.1 Deposition Sequence

In deposition sequence fine particles were deposited on the surface of catalyst in using suspension single-pass mode (Fig. 1) and then the flow was switched to multi-pass mode for reaction sequence (connector B in Fig. 1). The experiments were carried out at room temperature and atmospheric pressure using a 5.7-cm-i.d. Plexiglas column packed up to 34 cm bed height with 2.7-mm spherical Pd/Al₂O₃ catalyst. Palladium was chosen for its hydrogenation activity of reactants at room conditions.¹⁹ The properties of bed and reaction materials are shown in Table 1. The packing was maintained by means of a rigid stainless steel screen placed at the column bottom. The screen's mesh opening (rhombic shape, 0.65x1.3 mm²) was set to prevent collectors (i.e., packing elements) from crossing over while barely blocking the exiting flow of suspension. Kaolin, being a major component of the clay in Athabasca oil sand,²⁰ was added to kerosene which is chosen for its low vapor pressure, stability and chemical similarity with hydrocarbons.⁴ Kaolin powder was heated to remove any moisture before being added to the kerosene. Similarly, catalyst packing was heated in oven before being used to remove any moisture contents.

Prior to catalytic conversion, in-situ reduction of the alumina bed was carried out under hydrogen stream for 2 h to activate catalyst. Kaolin was sonicated in an ultrasonic cleaner prior to make suspension to avoid filter-cake formation. Direct addition of kaolin into kerosene would lead to formation of suspension with fine particles of several hundred micrometers in size which could cause

straining. This is commonly encountered where fines are larger than the pore constriction causing formation of filter cake as well as dramatic pressure drop. The suspensions were prepared with one gram of kaolin per liter of kerosene.

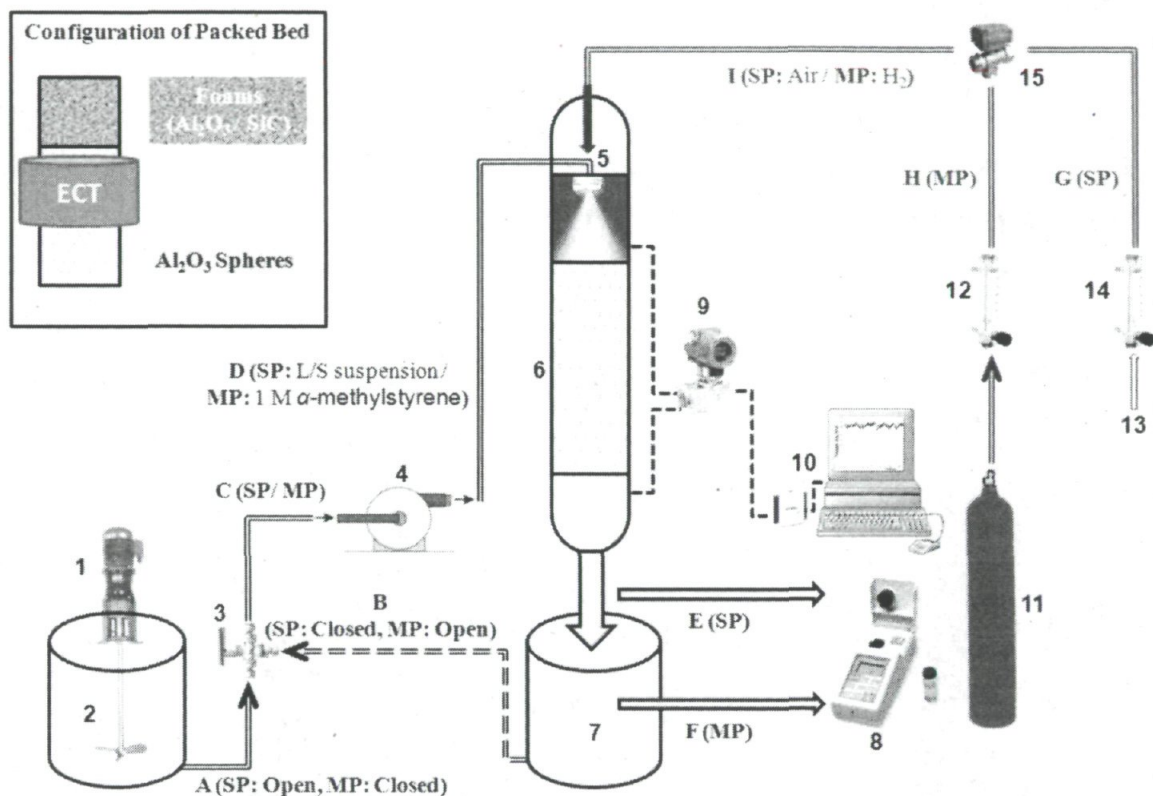


Figure 1 Schematic diagram of experimental setup (inset showing configuration of packed bed with foams and alumina spheres). Numeric and alphabet symbols represent the equipments and flow connections respectively. (1: Mixer, 2: Feed tank, 3: Two way valve, 4: Peristaltic Pump, 5: Gas-Liquid Spray Nozzle, 6: Trickle Bed Reactor, 7: Feed/ Storage tank, 8: Turbidimeter, 9: Differential pressure transducer, 10: Data acquisition system, 11: Hydrogen cylinder, 12: Hydrogen flow-meter 13: Air supply, 14: Air flow-meter, 15: Electronic switch valve, SP: Single Pass Deposition Sequence, MP: Multi Pass Reaction Sequence)

Optical microscopy analysis of the fines size distribution in the suspension revealed mean diameter³ of ca. $8\mu\text{m}$ which is compatible with the fine sizes found in actual trickle-bed reactors.⁵ Catalyst was immersed in kerosene for 30 min prior to experiments to achieve full wetting of bed and imbibitions of intra-particle porosity by the liquid.

The suspension was stirred in a feed tank, pumped to the column top and distributed through a spray nozzle to ensure even distribution of the suspension. To avoid the blockage of nozzle, as opening size was ca. 0.5 mm, special attention was paid to prevent the introduction of solid impurities into the feed

tank. The position of the nozzle was visually adjusted to ensure homogeneous distribution of the suspension across the whole cross section of the uppermost layer of the packed bed; a typical distance of 3 cm was used. Connecting pipes from the column to the pump and tanks were positioned as vertically as possible to avoid untimely deposition in the lines. The outlet concentration was measured each 30 min through sampling at the bed exit during deposition sequence to calculate the specific deposit using turbidimeter calibrated for the range of experiments. Air was allowed to enter through several small holes on the top of the bed to prevent preferential gas flows. After each experiment, the column was dismantled, and the particles were carefully washed with water and dried overnight in an oven (100-110°C) before subsequent use.

Table 1 Properties of reaction and bed material

| Property | Description |
|---------------------------|--|
| Reactants | α -methystyrene (l) + H ₂ (g) |
| Solvent | Kerosene |
| Fine particles | Kaolin |
| Catalyst | Pd (0.8 %w) |
| Catalyst support | Al ₂ O ₃ Spheres |
| Size (catalyst + support) | 2.7 mm |
| BET surface area | Fresh 112 m ² /g; cleaned after filtration 64 m ² /g |
| Bed specific surface area | 1355.5 m ² /m ³ |
| Porosity | 0.4 |

The pressure drop across the whole bed was recorded every 10 s. The amount of deposit inside bed, i.e., specific deposit, σ , which is mass of kaolin particles deposited per unit volume of vessel (empty reactor basis), was determined. In single-pass mode specific deposit was calculated from a mass balance around the bed. Two different tanks were used as shown in Fig. 1, one containing the pristine suspension (constant concentration, 1 g/L) and the other, a storage tank, where spent suspension leaving bed was collected after passing through a fabric (used as filter placed on top of storage tank). This latter filtered kaolin and clean kerosene was collected in tank which could be reused to make suspension. Specific deposit in single-pass is calculated as:

$$\sigma(t) = \int_0^t \frac{Q[C_{IN}(\tau) - C_{OUT}(\tau)]}{V_R} d\tau \quad (1)$$

Air was used as gas during single-pass mode and an electronic valve was programmed to shift from air to hydrogen flow to perform the reaction sequence. After achieving in single pass a target bed deposition, the suspension flow was shifted to multi-pass, i.e., inlet of the reactor was disconnected

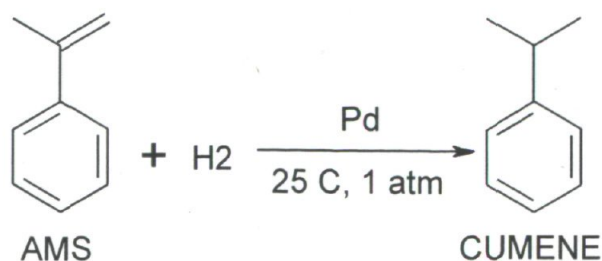
from reservoir (2) and connected to feed/storage tank (7) through the two-way valve (3) (connector B). Samples were taken from (7) during multi-pass to calculate the concentration of fine particles inside feed/storage tank before and after transition from air to hydrogen. The experiments were conducted at superficial velocities of air 0.0098 m/s, 0.31 m/s, hydrogen 0.0149 m/s and suspension at 0.00196 m/s coinciding with trickle-flow regime. Specific deposit during multi-pass is calculated through a mass balance around the feed/storage tank as:

$$\sigma(t) = [C_T(t=0) - C_T(t)] \frac{V_T}{V_R} \quad (2)$$

Electrical capacitance tomography (ECT) measurements were obtained using a twin-plane vertically-sliding 12 electrode-per-plane sensor with a DAM200E data acquisition system PTL300E type was utilized (Process Tomography Ltd.). Tomographic imaging is helpful to capture, without interference with the actual hydrodynamics, the evolving tomography at depths inside the bed which otherwise are inaccessible from mere wall scrutiny.⁹ ECT is also compatible with kerosene suspension, as used in our experiments.²¹ The two rows of electrodes, girdling circumferentially the column, were 50-mm high with guard electrodes 38-mm high placed immediately above and below. The measured capacitances allowed reconstructing permittivity images (32×32pixels per image) at different cross-sectional and longitudinal positions with sampling frequencies up to 100 Hz. A Tikhonov reconstruction algorithm was chosen to generate normalized permittivity images from the measured capacitances. Selection of this algorithm with regard to the filtration problem was discussed in recent works.^{20,21} In the calibration step, the measured lower- and upper-limit permittivity values enabled to set, respectively, the 0 and 1 limits of the normalized permittivities interval so that intermediate per-pixel normalized permittivity values in images during flow conditions can be computed.

1.2.2 Reaction Sequence

The reaction chosen for this study was hydrogenation of α -methylstyrene (AMS) to cumene over Pd/alumina catalyst.



This reaction has been studied extensively by a number of investigators²²⁻²⁶ and is known to proceed with a noticeable rate even at ambient temperature and atmospheric pressure. In catalytic conversion reaction, after achieving the desired specific deposit, single-pass mode was shifted to multi-pass mode. In multi-pass mode, the suspension was merely recirculated through the packed bed from, and into, one single feed/storage tank which contained solution of 1M α -methystyrene/kerosene + kaolin/kerosene suspension (1g/L). Samples were taken from the feed/storage tank after each 10 min for analysis of conversion and to calculate the specific deposit while using multi-pass mode to get the overall specific deposit. Samples were analyzed using a Hewlett-Packard 5890 Series II gas chromatograph (30 m x 32 mm x 25 μ m model DB-5MS packed column). Peak areas of the compound of interest were normalized relative to toluene (internal standard) and converted to concentration via calibration curves generated experimentally following the internal standard technique.

1.2.3 Filtration with Foams

The experiments for hydrodynamic studies of trickle bed during filtration with/without solid foams as upstream guard packing were carried out at room temperature and atmospheric pressure.

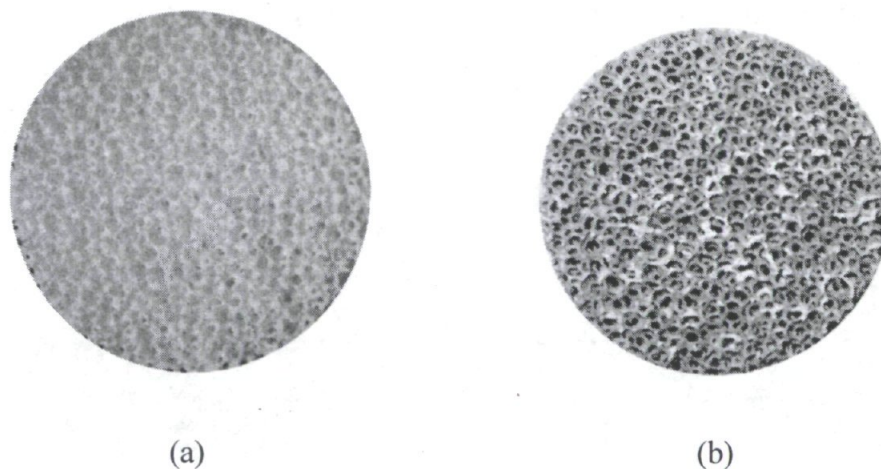


Figure 2 (a) Al_2O_3 (b) SiC Foam (20 ppi)

Alumina (Al_2O_3) and SiC foams (Fig. 2) were used having pore size 20 ppi (pores per inch). Foams were placed on top of the trickle bed (height 34 cm). Suspension of kaolin/kerosene (1 g/L) and air were the test fluids, flowing co-currently downstream through packing in single-pass mode. Pressure drop was measured across the bed by means of transducers and samples were taken at bed outlet to calculate the mass of kaolin retained inside the bed during filtration in single-pass mode from the mass balance around the reactor. ECT sensor was installed to monitor the evolution of deposition.

Clean flow experiments were conducted prior to filtration with spherical γ -alumina particles to monitor liquid distribution inside TBR with/without upstream foams. Liquid saturation inside bed was monitored by placing ECT sensor at top and bottom of TBR for different air and liquid superficial velocities. Filtration experiments were conducted first without foams to measure pressure drop and specific deposit and to monitor the deposition structure and then carried out with foams under similar operating conditions. ECT sensor was placed right after the foams at top of the TBR to assess the effect of foams on normalized permittivity inside TBR as shown in Fig. 1 (inset). Filtration experiments were carried out at $U_{Air} = 0.0098$ m/s, 0.15 m/s and liquid suspension at $U_L = 0.0013$ m/s, 0.00196 m/s.

After each experiment, the column was dismantled, and the particles and foams were washed with water and dried overnight in an oven before subsequent use. Special care was given while cleaning the foams because all the liquid used during cleaning was collected in the storage which was later filtered to weigh the mass of kaolin retained inside the foams. Specific deposit inside TBR was calculated as:

$$\sigma(t) = \frac{\text{Total gm. of kaolin retained inside TBR \& foam(S) - gm. of kaolin retained inside foam(s)}}{V_R} \quad (3)$$

Filtration experiment was also conducted with column packed with Al_2O_3 solid foams (4 modules) to monitor the structure of deposition inside alumina foams. ECT sensor was placed at top of column right at the start of foams; at distance of 2.5 cm from nozzle. Air and kaolin/kerosene suspension were the testing fluids. Experiment was carried out at superficial velocities of air 0.15 m/s and of suspension 0.00196 m/s.

1.3 Results and Discussion

1.3.1 Operating Conditions for Deposition Sequence

As long runs are required to build up deposits which consume large amounts of gas and because of safety issues, it was not feasible to operate with hydrogen all through the runs. It is important thus to make sure that the deposition layer keeps unchanged during transition from air to hydrogen flow. Experiments were conducted to adjust accordingly the operating conditions (i.e., gas and liquid superficial velocities). First clean test (i.e., fines-free kerosene) was performed then filtration test was conducted under similar operating conditions to analyze their effect on deposition.

In the first test air and liquid superficial velocities were adjusted to achieve the same pressure drop before and after transition from air to hydrogen in the packed bed to minimize the disturbance. Figs. 3a,b show pressure drop and liquid saturation curves during transition from air to hydrogen in clean flow at $U_{Air} = 0.0098$ m/s, $U_g = 0.0149$ m/s and $U_L = 0.00196$ m/s. The saturation results were obtained

via ECT imaging. The procedure to perform experiments and calculations was explained in details in our previous studies.²² It was observed that using these operating conditions same pressure drop and liquid saturation was achieved before and after transition from air to hydrogen with a few-seconds transient perturbation in bed hydrodynamic parameters. The same operating conditions were then tested for the deposition sequence in single-pass mode. After achieving a desired deposition, single-pass was shifted to multi-pass and air was switched to hydrogen. ECT sensor was placed at the top of the bed to monitor the influence of transition. ECT calibration procedure in the course of filtration run to distinguish the deposition pattern could be found in our previous studies.²² Concentration of fine particles inside the feed/storage tank during multi-pass was monitored by taking samples 1 min before and after transition.

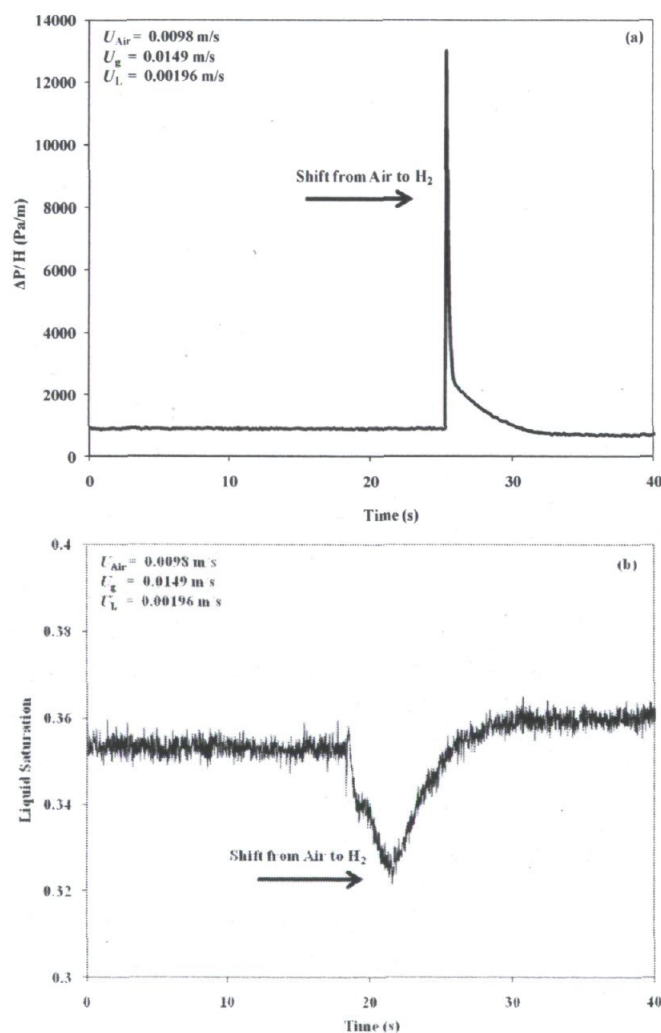


Figure 3 Pressure drop, (a) and liquid saturation, (b) curves during transition from air to hydrogen in clean flow while using low velocity of air ($U_{Air} = 0.0098$ m/s, $U_g = 0.0149$ m/s, $U_L = 0.00196$ m/s).

Fig. 4a shows that normalized permittivity decreased after transition. As explained elsewhere²² the total permittivity results from adding the permittivity of each phase (i.e., gas, liquid, bed and deposit); therefore, the increase or decrease in permittivity could be an evidence of deposition or detachment. The dip in Fig. 4a shows that after shift from air to hydrogen some of the deposit built up in single-pass was detached. Re-deposition of detached fines could block the flow passage and cause liquid accumulation. Therefore, the average bed permittivity starts to increase reaching eventually the limit that can force the accumulated fines to leave the bed (Fig. 4a). Consequently, the permittivity drops to a quasi-steady lower level. This could also be verified by measuring the concentration of fine particles inside feed/storage tank (Fig. 4b). The concentration after transition has increased beyond the initial feed concentration of 1 g/L confirming that deposit was partially removed from the bed. Hence setting the operating conditions on the basis of the clean flow adjustments (Fig. 3) is not reliable to perform catalytic conversion studies with undisturbed deposit structures after switching from air to hydrogen flow.

In a next step, high air superficial velocity was used during the deposition sequence ($U_{\text{Air}} = 0.31$ m/s, $U_g = 0.0149$ m/s, $U_L = 0.00196$ m/s) to assess the possibility of stabilizing deposition layer. Figs. 5a,b show normalized permittivity in the bed and concentration of fines inside the feed/storage tank before and after shift from air to hydrogen during multi-pass mode. It can be seen that normalized permittivity did not decrease after transition. In fact an increase has been noticed which is due to the change from high air superficial velocity to low hydrogen superficial velocity. Decrease in drag force acting on liquid causes the increase in liquid saturation and normalized permittivity (Fig. 5a). Unlike the previous strategy, samples taken from feed/storage tank show that fines concentration slightly decreased because of fines deposition in the bed from the recirculating suspension (Fig. 5b).

The results shows that when low air superficial velocity was used during the deposition sequence then fine particles are loosely attached on the surface of collector and sudden flow perturbation could detach them. Filtration at high air superficial velocity and then shift to hydrogen revealed that fines are more compactly attached on the collectors' surface and that transition has a minor impact on morphology of deposition. Thus it will be applicable to perform the catalytic conversion reaction to analyze the effect of deposition on conversion. In all catalytic conversion experiments high superficial velocities for air were used (0.15 m/s & 0.30 m/s) during deposition sequence.

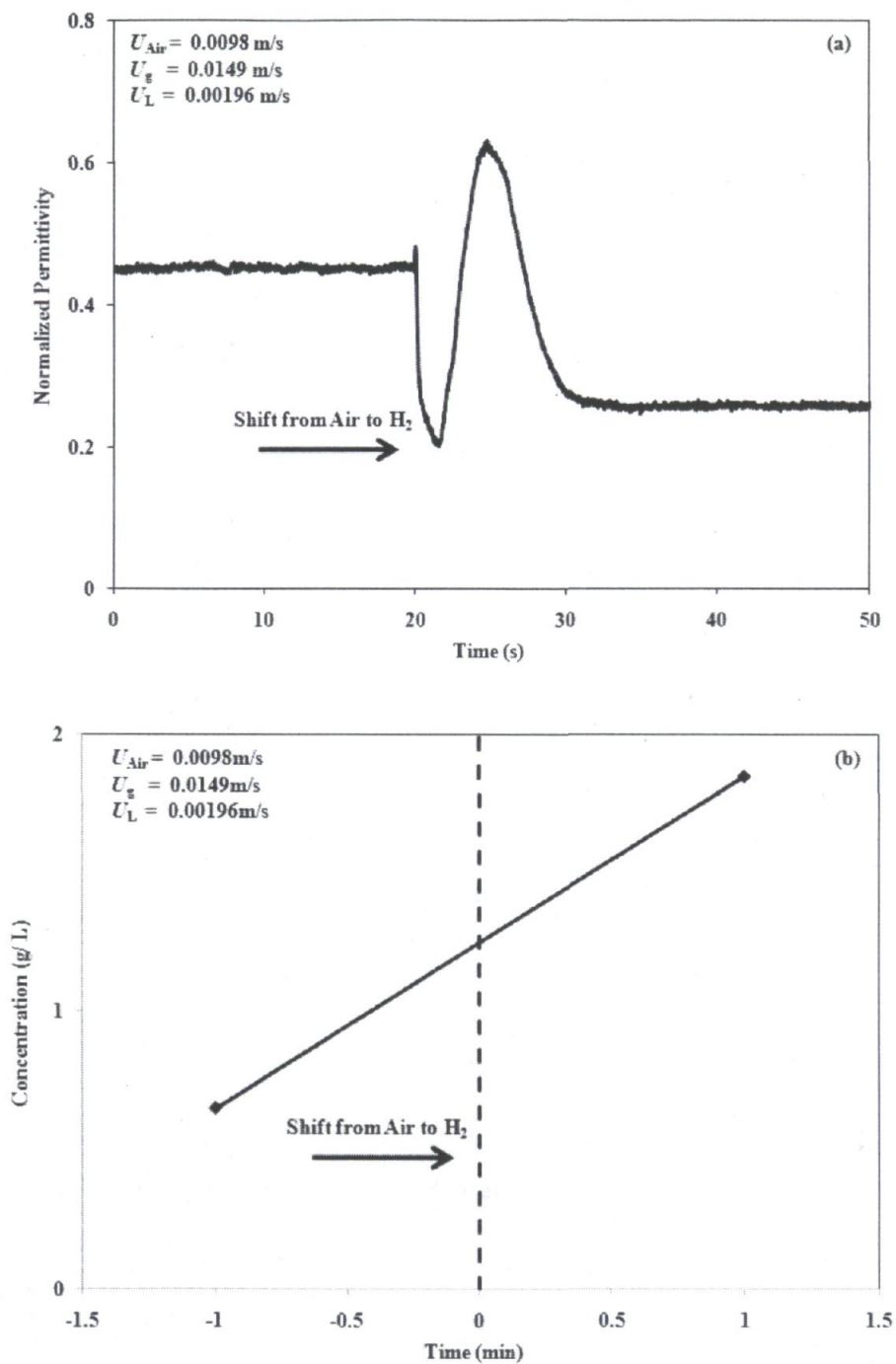


Figure 4 (a) Normalized permittivity vs. time before and after transition from air to hydrogen (b) Concentration of fine particles in feed/storage tank during multi-pass 1 min before and after transition from air to hydrogen, $U_{air} = 0.0098$ m/s, $U_g = 0.0149$ m/s and $U_L = 0.00196$ m/s.

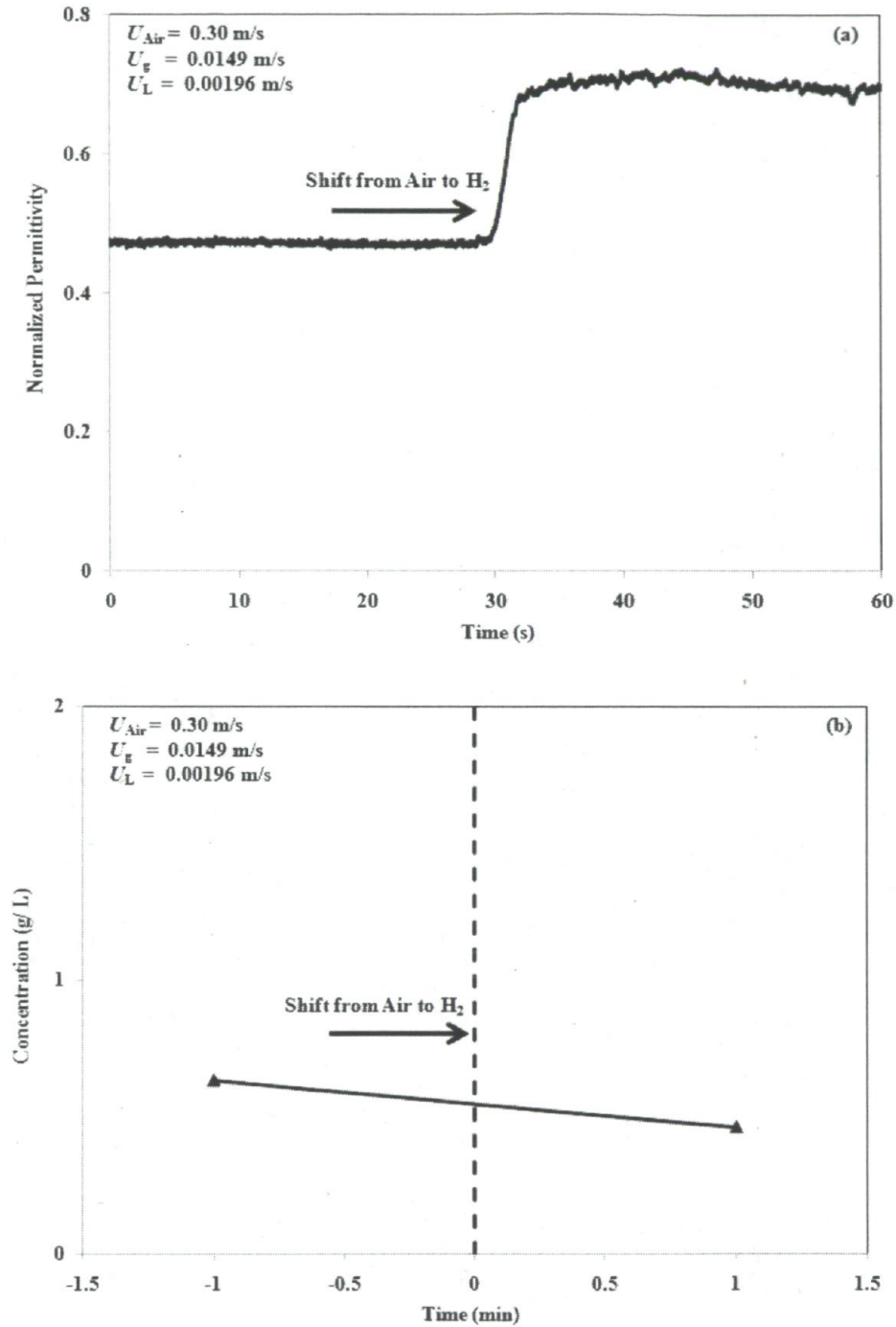


Figure 5 (a) Normalized permittivity vs. Time before and after transition from air to hydrogen (b) Concentration of fine particles in feed/storage tank during multi-pass 1 min before and after transition from air to hydrogen, $U_{air} = 0.30$ m/s, $U_g = 0.0149$ m/s and $U_L = 0.00196$ m/s.

The results shows that when low air superficial velocity was used during the deposition sequence then fine particles are loosely attached on the surface of collector and sudden flow perturbation could detach them. Filtration at high air superficial velocity and then shift to hydrogen revealed that fines are more compactly attached on the collectors' surface and that transition has a minor impact on morphology of deposition. Thus it will be applicable to perform the catalytic conversion reaction to analyze the effect of deposition on conversion. In all catalytic conversion experiments high superficial velocities for air were used (0.15 m/s & 0.30 m/s) during deposition sequence.

1.3.2 Catalytic Reaction

The purpose of catalytic conversion with/without filtration was to investigate the effect of deposition on reaction conversion. First, clean test (i.e., fines-free kerosene) was carried out to compare with reaction experiments under filtration. Similar operating conditions for clean and filtration experiments were opted ($U_{Air} = 0.30$ m/s, $U_g = 0.0149$ m/s and $U_L = 0.00196$ m/s). After achieving the desired specific deposit single-pass mode was shifted to multi-pass mode to carry out the reaction while using hydrogen as gas. In multi-pass mode inlet of pump was connected to feed/storage tank containing 1 g/L kaolin/kerosene suspension. In recirculation mode after uptake of fines from the reservoir as there was no further addition of fines bed specific deposit as well as pressure drop started to achieve a plateau indicating a constant deposition layer. After reaching this stage, α -methylstyrene was added in reservoir (1 M) to carry out the reaction. Figs. 6a,b show the time evolution of specific deposit and pressure drop in both single- and multi-pass mode. Fig. 6a depicts that specific deposits indeed plateaued confirming the deposits' invariance in multi-pass mode. Plugging phenomena and build-up of pressure drop in trickle bed reactor has been investigated and explained in details in our previous studies.^{3-7,9,10} Catalytic conversion experiments were carried for 3 different values of specific deposits ($\sigma = 17.1, 34.7$ and 56.4 kg/m³). Fig. 6c shows the effect of deposition on reaction conversion under filtration. It has been noticed that up to certain level of deposition there is no significant impact of deposition on conversion but as specific deposit has been increased there is significant drop in conversion ($\sigma = 34.7$ and 56.4 kg/m³). Fig. 6c shows some drop in conversion for clean test (i.e., fines-free kerosene) performed after filtration experiments as compared to conversion achieved with new catalyst. This suggests that part of the catalyst activity is permanently lost due to the irreversible deposition of fine particles on the active sites.

Another set of experiments was conducted under same operating conditions ($U_{Air} = 0.30$ m/s, $U_g = 0.0149$ m/s, $U_L = 0.00196$ m/s) and almost same specific deposits ($\sigma = 17, 33.2$ and 53 kg/m³). Fig. 7

shows further drop in conversion. Clean test conducted after filtration experiments shows that drop in catalytic performance is more significant as compared to previous series of experiments.

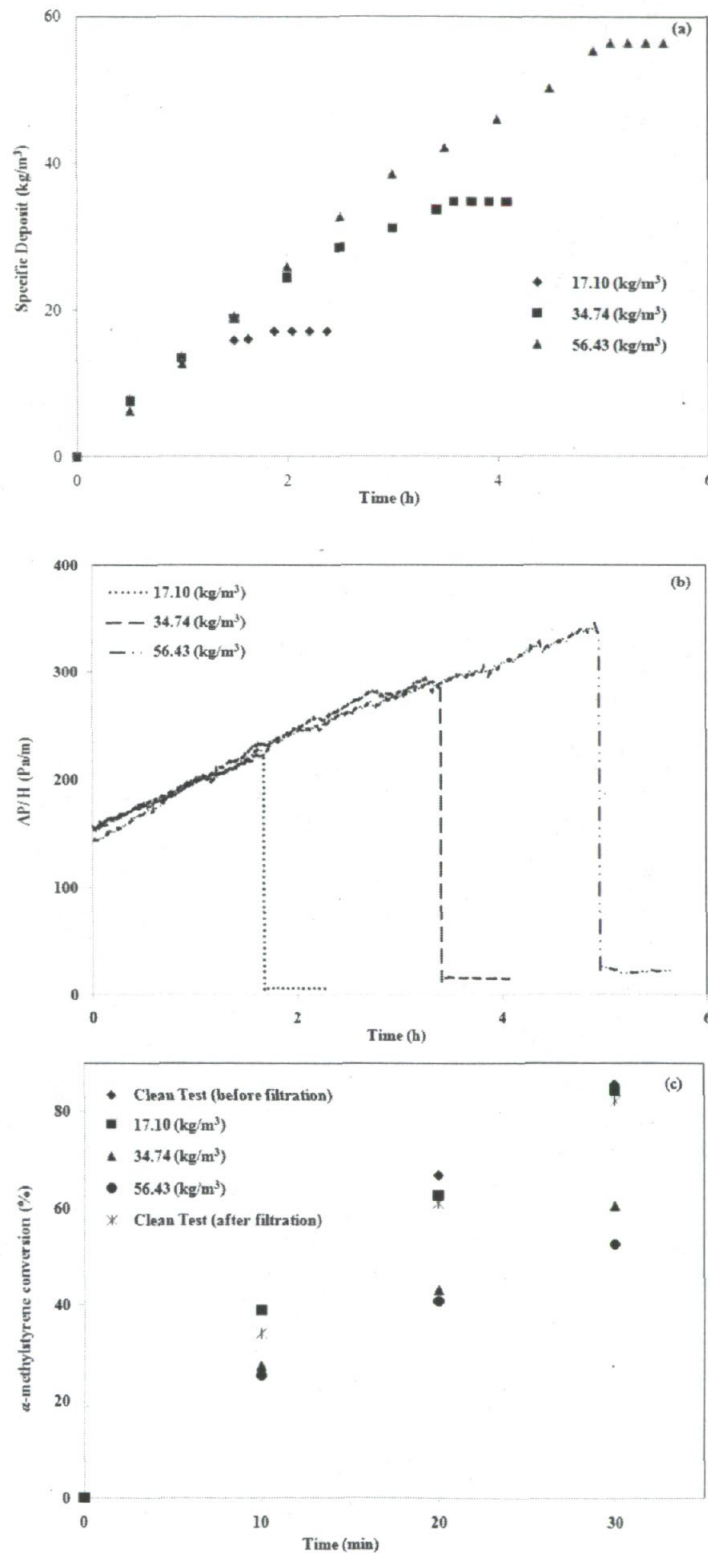


Figure 6 (a) Specific deposit vs. time during filtration (single-pass and plateau with multi-pass), (b) pressure drop vs. time during filtration at different specific deposits in TBR (c) Effect of deposition on catalytic conversion of α -methylstyrene with/without filtration, $U_{\text{Air}} = 0.30$ m/s, $U_g = 0.0149$ m/s, $U_L = 0.00196$ m/s.

These results show that during filtration catalyst loses its performance and activity due to physical blockage of active sites. Less active sites being reached by hydrogen as externally growing deposits cause mass transfer limitations forcing H_2 diffusion through the tortuous paths of the evolving deposits. Some of fine particles may enter inside the catalyst pores and physically block access to liquid/gas reactants which ultimately cause the loss in conversion during catalytic reaction. EDS analysis of catalyst after filtration experiments confirms the presence of silica on the catalyst surface which is not present on the surface of original catalyst (see supporting information section, Fig. SI-1). Since silica is one of the components of kaolin, this could be an indication of its presence even after deposition removal. Also, measured BET surface area after cleaning alumina particles subsequent to filtration runs led to a drop from $112 \text{ m}^2/\text{g}$ to $64 \text{ m}^2/\text{g}$ (Table 1).

1.3.2.1 Effect of Compact and non-Compact Deposition

Fig. 8 shows the catalytic conversion ($U_g = 0.0149 \text{ m/s}$, $U_L = 0.00196 \text{ m/s}$) during the reaction sequence for almost the same bed specific deposit ($\sigma = 33.2$ and 35.5 kg/m^3) using different air superficial velocities ($U_{\text{Air}} = 0.30$ and 0.15 m/s) during deposition sequence. It shows conversion is higher during reaction after achieving deposition at $U_{\text{Air}} = 0.15 \text{ m/s}$ as compared to conversion after achieving deposition at $U_{\text{Air}} = 0.30 \text{ m/s}$.

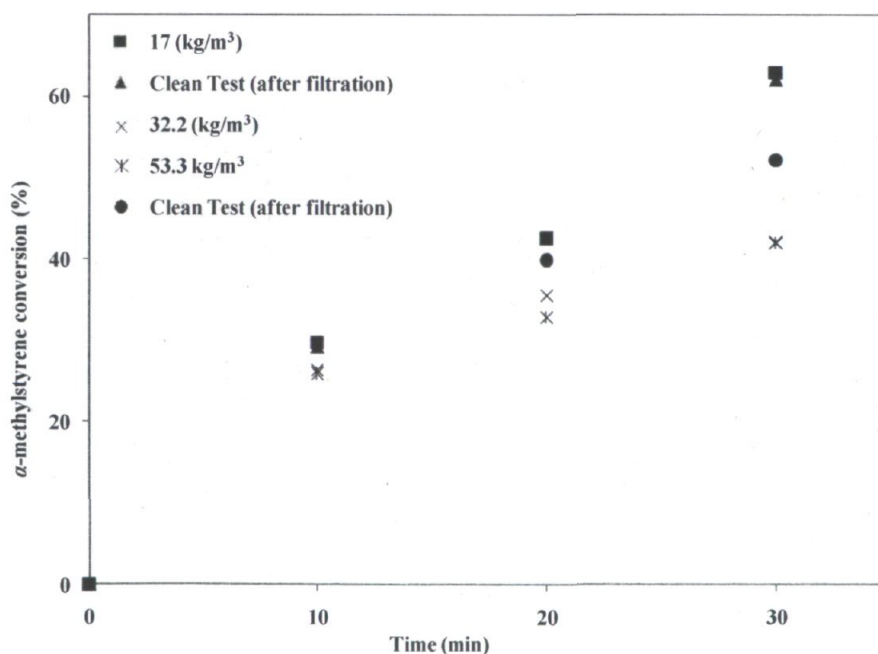


Figure 7 Effect of deposition on catalytic conversion of α -methylstyrene with filtration, alternate set of experiments, $U_{\text{Air}} = 0.30 \text{ m/s}$, $U_g = 0.0149 \text{ m/s}$, $U_L = 0.00196 \text{ m/s}$.

A plausible explanation is that the deposited layer over the catalyst surface is more compact at higher air velocity which may limit access of reactants to catalyst surface affecting the rate of conversion. This compaction phenomenon was verified by experiments conducted with injections of an electrical conductivity improver (ECI) during filtration in TBR packed with spherical alumina particles. ECI injections were shown to modify the zeta potential of the collector-deposit assemblage inducing detachment by prompting strong repulsive forces between fines.¹⁰

Different air superficial velocities (0.31 and 0.0098 m/s) were used for deposition sequence in TBR to achieve same localized specific deposit and ECT sensor was installed to monitor the bed normalized permittivity during the injection of ECI (for 10 seconds). ECI diffusion into the deposition layer will cause surface charge changes. Strong repulsive forces between surfaces charged alike will prompt detachment.¹⁰ If the deposited layer over the surface of alumina is very compact (at high gas velocity) it will limit penetration of ECI into deposits reducing detachment. An illustration of this mechanism has been included in the supporting information section (Fig. SI-2). Fig. 9 shows normalized permittivity of bed during ECI injection. It could be noticed that normalized permittivity after detachment caused through ECI injection is lower when deposition was achieved at low air superficial velocity ($U_{Air} = 0.0098$ m/s) as compared to when same localized specific deposit was achieved at high superficial velocity ($U_{Air} = 0.30$ m/s) indicating that lesser detachment occurred when deposition layer was generated using higher gas superficial velocity. During ECI injection, gas velocity was cut to maintain similar liquid saturations. This is reasonable with the low to moderate deposition levels generated under different operating conditions which do not significantly impact liquid saturation. To confirm this, liquid saturation was measured in separate filtration experiments ($U_{Air} = 0.30$ m/s and 0.0098 m/s) as well as in clean test using drainage technique at constant liquid velocity, $U_L = 0.00196$ m/s.

Same overall specific deposit (17 kg/m^3) was achieved for different air velocities during deposition sequence (bed height = 80 cm). After achieving desired specific deposit gas flow was stopped and liquid flow was allowed to flow till bed achieved stable permittivity. After approaching this stage liquid flow was turned off too and liquid was collected at the outlet of bed while letting the bed drain. Liquid holdup measured during filtration tests were 0.125 and 0.128 respectively and during clean test 0.122 indicating no significant change in liquid holdup inside bed.

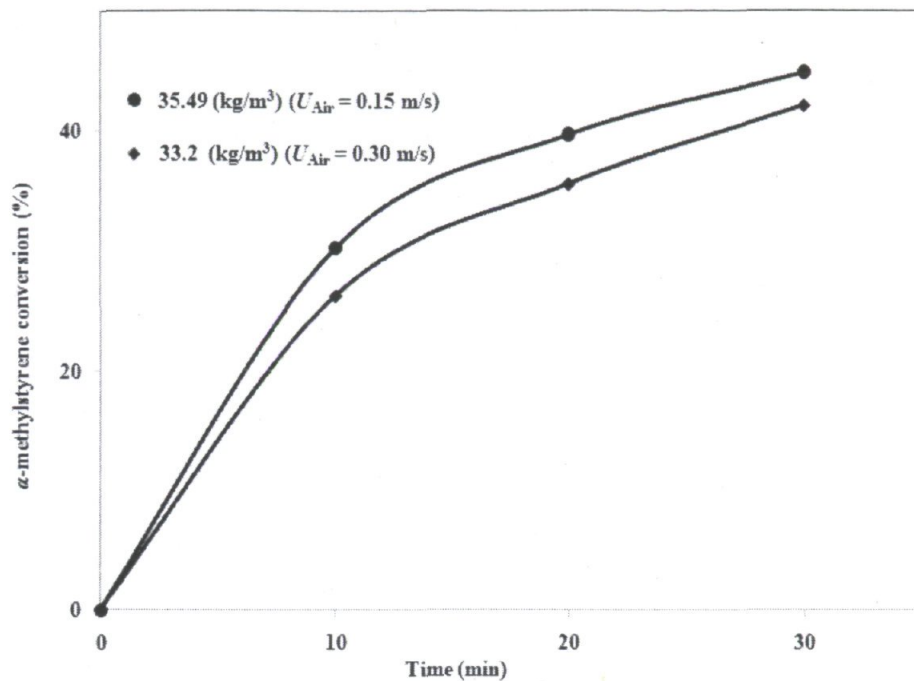


Figure 8 Catalytic conversion vs. time at hydrogen and liquid superficial velocities ($U_g = 0.0149$ m/s, $U_L = 0.00196$ m/s) and at different air superficial velocities ($U_{Air} = 0.30$ m/s and 0.15 m/s) during deposition sequence to achieve almost same specific deposit ($\sigma = 33.2$ kg/m³ and 35.5 kg/m³).

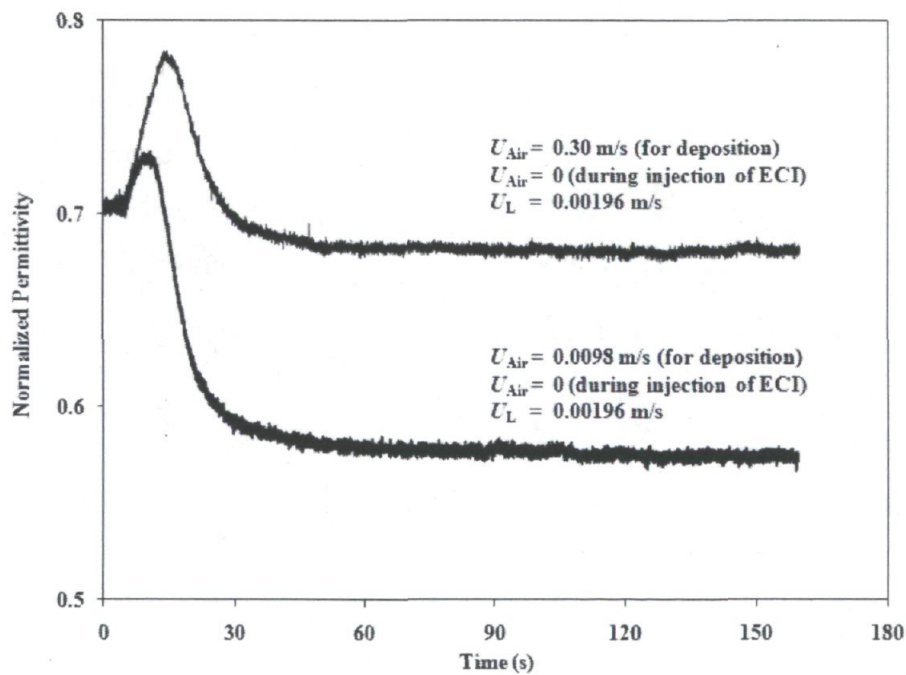


Figure 9 Normalized permittivity with time during impulsion of ECI after achieving same localized specific deposit at high and low U_{Air} (0.30 m/s and 0.0098 m/s) for constant $U_L = 0.00196$ m/s.

1.4 Filtration with Foams

It was illustrated that higher deposition inside the bed will result in lower conversion. It was speculated that the presence of a guard section before the packed bed could reduce the extent of deposition in the chemically active bed and prevent drastic conversion drop due to the deposit barrier. Since solid foams exhibit a high porosity, it may capture significant amount of fine particles without bringing about drastic bed pressure drop increases. The experiments were carried out with foams to assess their potential ability to act as upstream guards in TBR. Two types of foams were used during these experiments, alumina (Al_2O_3) and silicon carbide (SiC) solid foams having same specifications (20 ppi, 15 cm length). The purpose of using foams as upstream guards was to capture the kaolin particles from suspension to reduce their downstream deposition and pressure drop rise inside the catalyst packed bed and compare the capability to capture fine particles of these two kinds of foams. The presence of foams as upstream guards did not play any significant role in initial pressure drop values. ECT sensor was placed at the top of the packed bed (right after the foam module(s)) to monitor the deposition structure and bed normalized permittivity.

1.4.1 Liquid Distribution in TBR in Clean Flow

Prior to performing filtration tests, clean bed experiments were carried out to observe the effect of foams on the liquid distribution pattern in TBR. Calibration for tomography measurements was performed for a drained-pretreated bed as zero reference point (blue) and a bed flooded with kerosene as 100% reference point (red) to compute liquid saturation during two-phase flow. ECT measurements were taken once at top of packed bed of alumina spheres right after foams and then at bottom of bed (bed height = 80 cm). Two foam modules (15 cm long) were used upstream during the clean flow experiments at a distance of 2.5 cm from nozzle.

Fig. 10 shows liquid distribution along the radius of trickle bed reactor during clean flow without upstream foams at different air superficial velocities $U_{\text{Air}} = 0, 0.0098, 0.616, 0.15, 0.30$ m/s and $U_L = 0.0013$ m/s. Liquid saturation curves show more liquid in the middle of the bed at the top. At the bottom side the bed self-correcting distribution leads to more uniform liquid distribution. At high gas superficial velocity more uniform liquid distribution could be observed especially in the bed bottom section. This is because at low velocity it is easy for gas to flow through the available void space, whereas for higher velocities, a competition sets on between gas and liquid to occupy space. At high superficial velocity, gas exerts more shear force on the liquid to flow also through the space originally occupied by the liquid which ultimately results in more uniform distribution²⁷⁻²⁹ while fluids progress downwards ($U_{\text{Air}} = 0.30$ m/s). Fig. 11 shows radial distributions of liquid in TBR during clean flow

with Al_2O_3 and SiC upstream foams at different gas (air) velocities ($U_{\text{Air}} = 0, 0.0098, 0.0616, 0.15, 0.3$ m/s) at constant liquid (kerosene) velocity ($U_L = 0.0013$ m/s). ECT sensor was placed at top of TBR (bed height = 80 cm) right after foams and close to bottom. It shows lesser liquid irrigation is experienced in the center of the bed in case of Al_2O_3 foams which is not the case when SiC foams were used. The SiC foams reveal similar behavior with respect to experiments performed in trickle bed without foams. One of Al_2O_3 foams was dissected to observe the foam structure from inside. It revealed that foam cells in the center are blocked as a result of the foam synthesis protocol (Fig. 12) which is the reason that liquid saturation curves at top of bed show more liquid presence away from the bed center. No major blockage was noticed in SiC foams. At bottom side of bed liquid is more uniformly distributed along the radius of bed especially at high air superficial velocity which means bed is self-correcting which is more visible when SiC foams were used upstream.

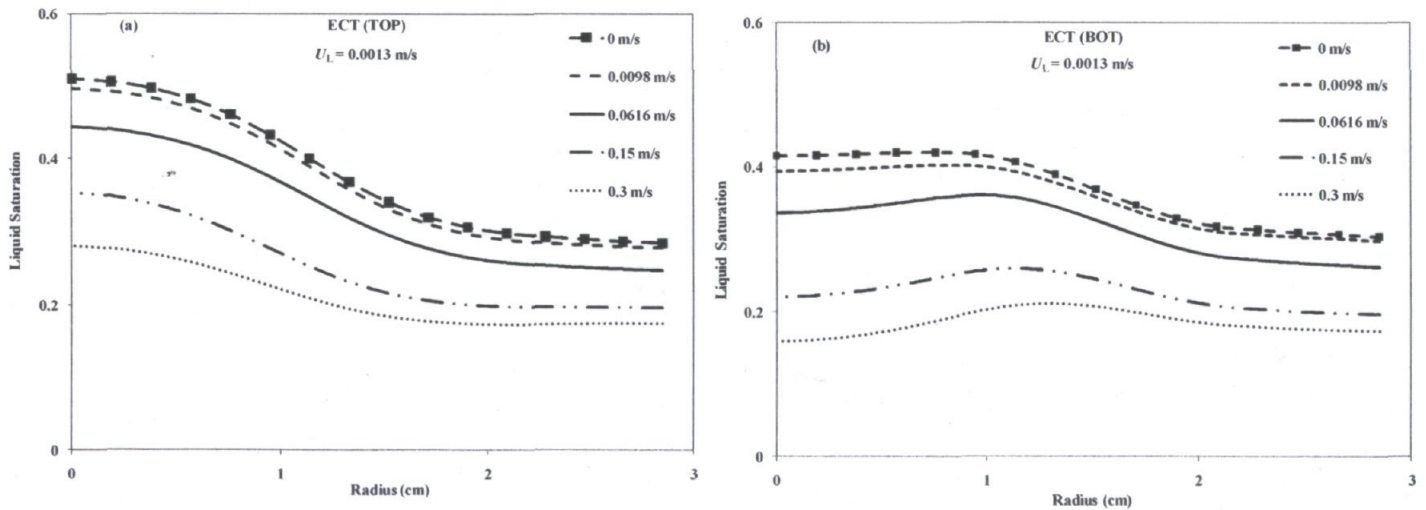


Figure 10 Effect of different gas velocities ($U_{\text{Air}} = 0, 0.0098, 0.0616, 0.15$ and 0.3 m/s), at constant liquid velocity ($U_L = 0.0013$ m/s) on radial liquid distribution in TBR without upstream foams, bed height = 80 cm. ECT was placed at top (a) and bottom (b) 39 cm apart from each other.

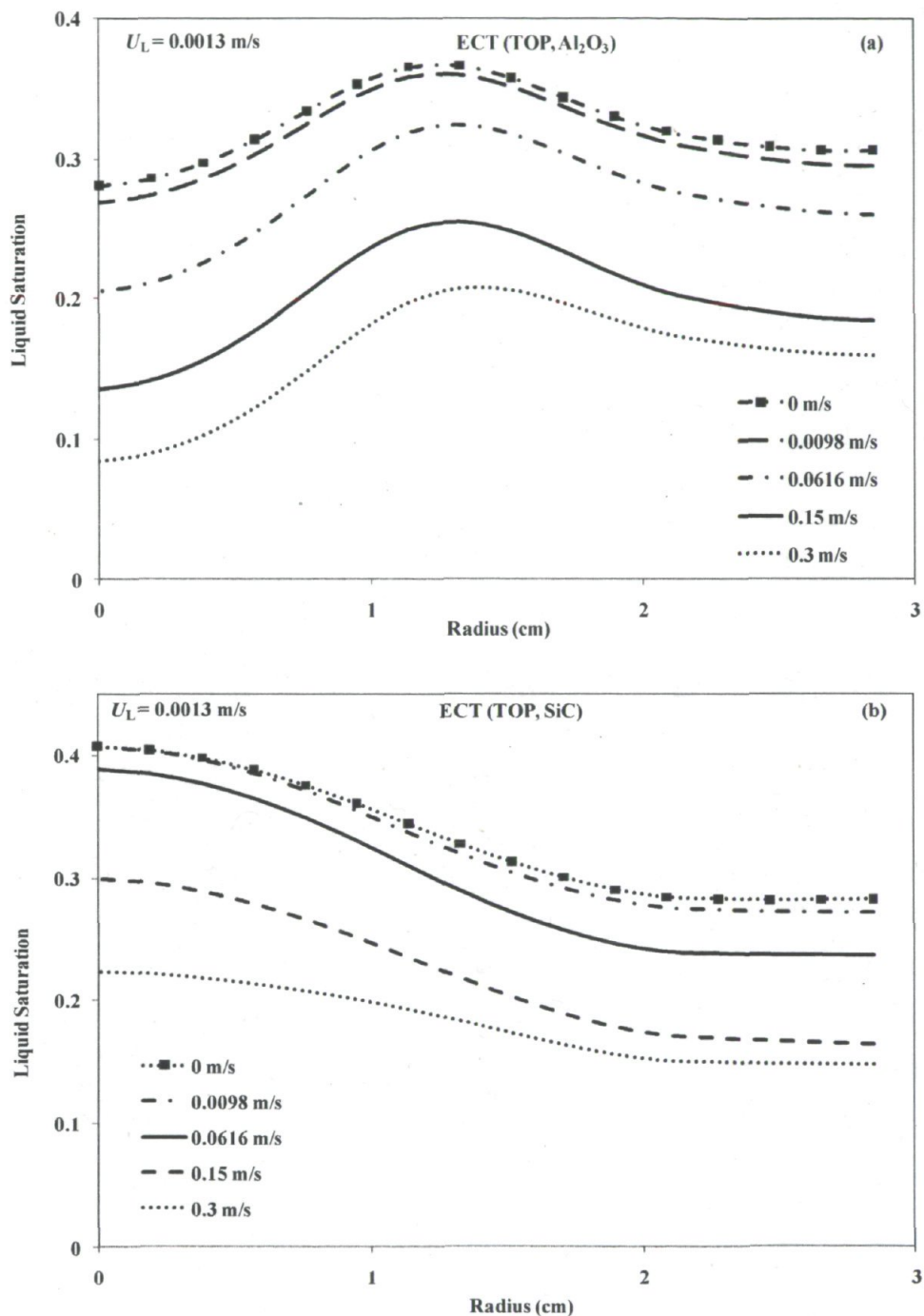


Figure 11 Radial distribution of liquid in TBR during clean flow with two Al₂O₃ and SiC upstream foam modules at different air velocities. ECT was placed at top (a,b) right after foam modules and at bottom (c,d) of column ($U_{Air} = 0, 0.0098 \text{ m/s}, 0.0616 \text{ m/s}, 0.15 \text{ m/s}$ and 0.3 m/s) at $U_L = 0.0013 \text{ m/s}$.

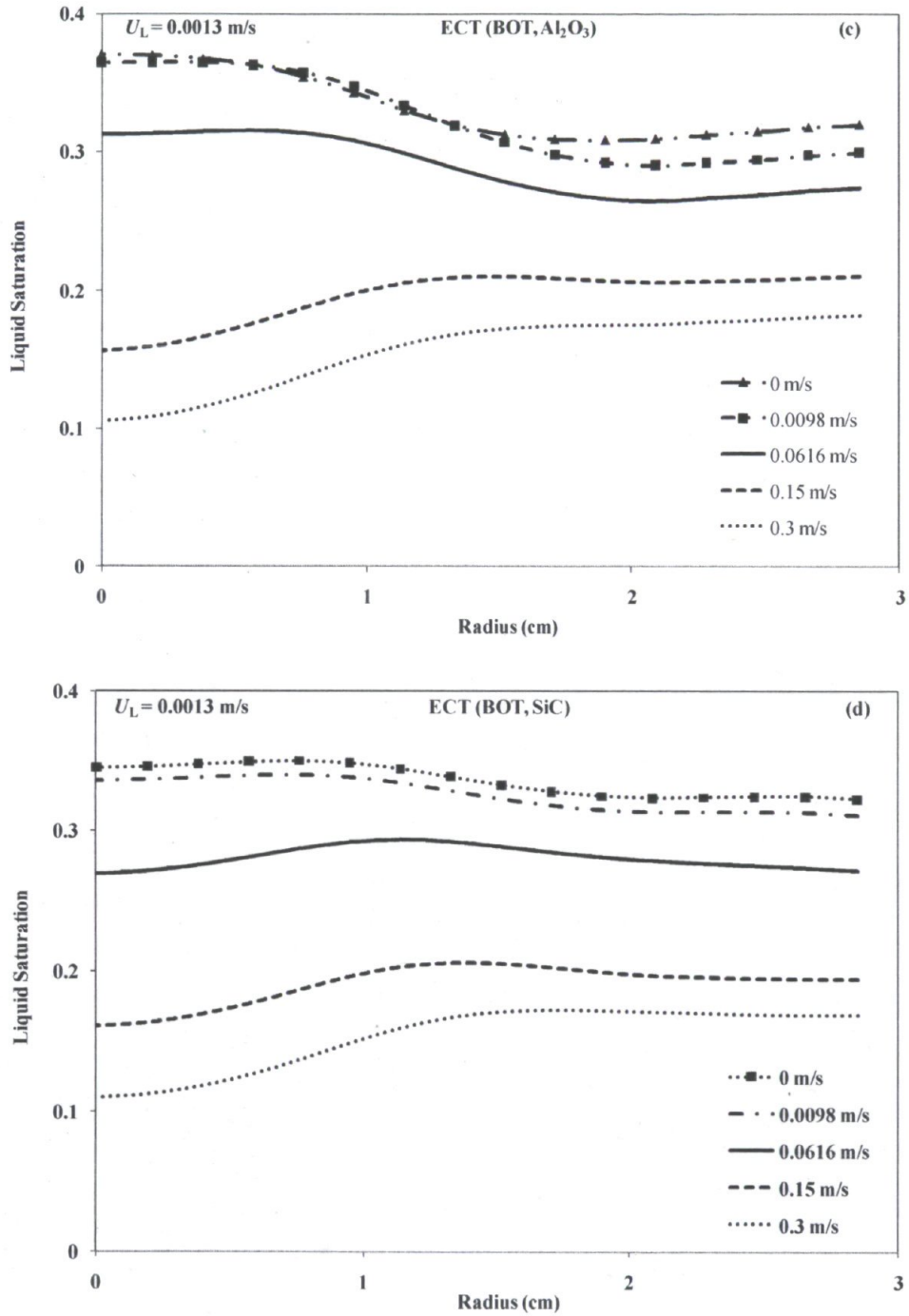


Figure 12 Continued.

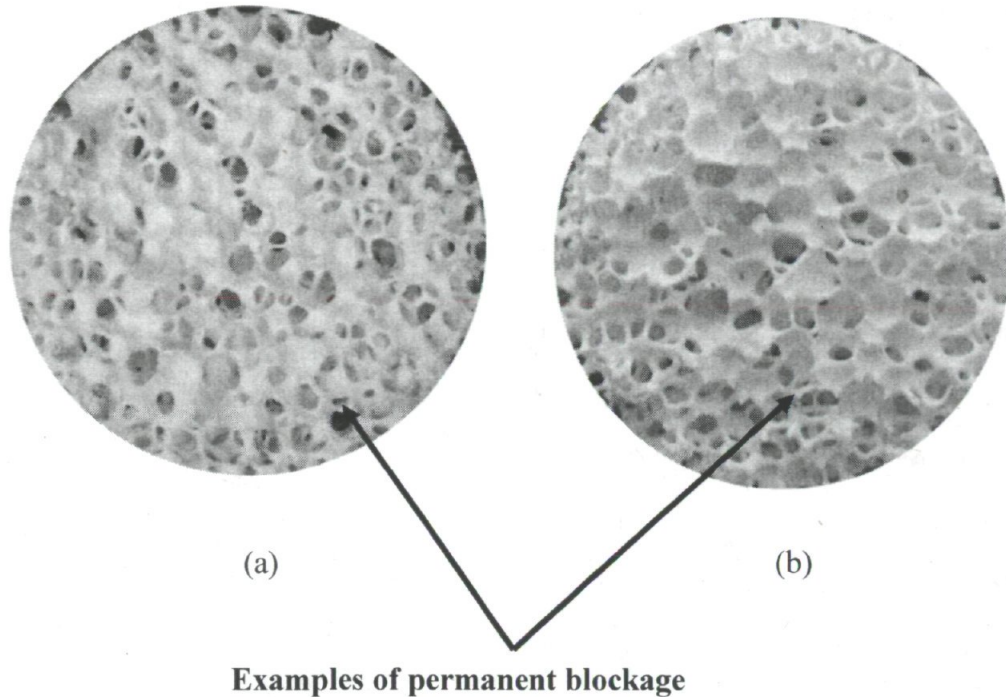


Figure 13 Inside view of Al_2O_3 solid foam after slicing at (a) 5 cm (b) 10 cm showing permanent blockage.

1.4.2 Filtration Experiments

Filtration experiments were carried out with Al_2O_3 and SiC foams as upstream guards to investigate their impact on deposition of fine particles in TBR at different air and suspension superficial velocities. ECT sensor was placed right after the foam blocks as shown in Fig. 1. Figs. 13a-c show *overall* bed pressure drop during filtration with/without foams as upstream guards ($U_{\text{Air}} = 0.0098, 0.15$ m/s and $U_L = 0.0013, 0.00196$ m/s). It is observed that pressure drop decreased when foams were used, as a fraction of fines were captured by them. Fig. 13a depicts that using two alumina blocks, pressure drop remained constant for a while (~ 1 h) indicating that bed morphology was not altered significantly due to high foam porosity. Fig. 13a also shows the decline in pressure drop as well as specific deposit with increase in number of foam blocks. Filtration test with SiC foams as upstream guards reveals that capability of SiC foams to capture fine particles was not as good as alumina foams. It can be seen that for the first 1.5 h pressure drop follows the same trend as TBR run without upstream guard indicating minor contribution of SiC foam to capture fine particles.

Fig. 13b shows the time evolution of bed pressure drop in the course of filtration with/without upstream foams at $U_{\text{Air}} = 0.15$ m/s and $U_L = 0.00196$ m/s. It is seen that with the increase of gas superficial velocity, the capture ability of SiC foams has been improved; however, two SiC foams captured less fines than on single Al_2O_3 block. Fig. 13c shows bed pressure drop profiles with/without foams at U_{Air}

= 0.15 m/s and $U_L = 0.0013$ m/s. The ability of foams to capture fines has decreased at lower liquid superficial velocity. Since the nozzle bed distance was not changed, suspension distribution deteriorates. The entire available surface does not contribute to the capture process resulting in higher specific deposit in the packed section. To investigate the impact of foams on deposition in TBR with/without upstream guard foams, ECT was used in order to compare the normalized permittivity of TBR with/without foams ($U_{Air} = 0.15$ m/s, $U_L = 0.0013$ m/s).

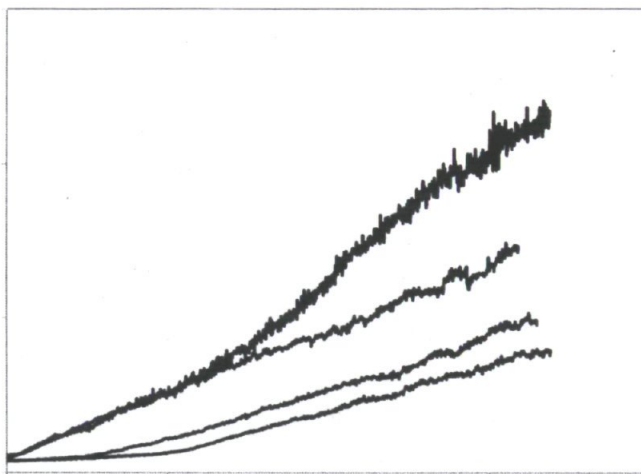


Figure 13 Pressure drop across TBR during filtration with/without foams as upstream guards at (a) $U_{Air} = 0.0098$ m/s and $U_L = 0.00196$ m/s. (b) $U_{Air} = 0.15$ m/s and $U_L = 0.00196$ m/s (c) $U_{Air} = 0.15$ m/s and $U_L = 0.0013$ m/s.

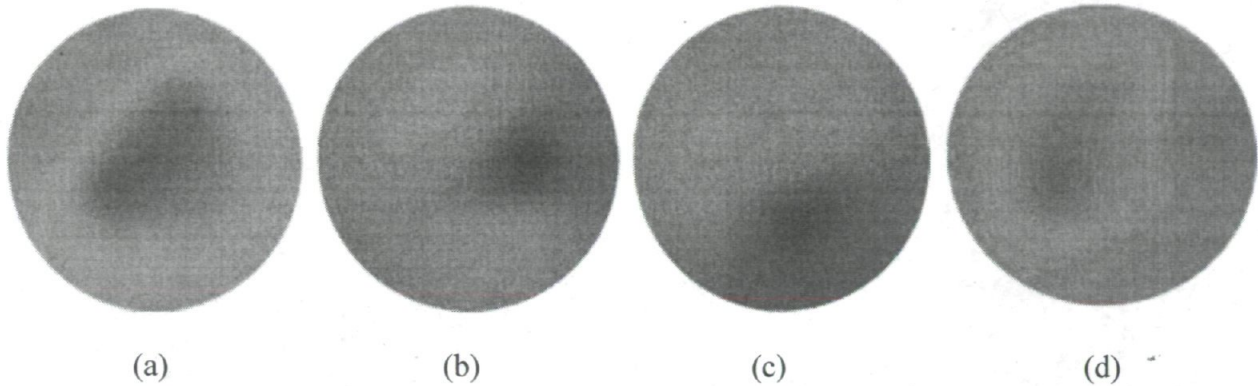
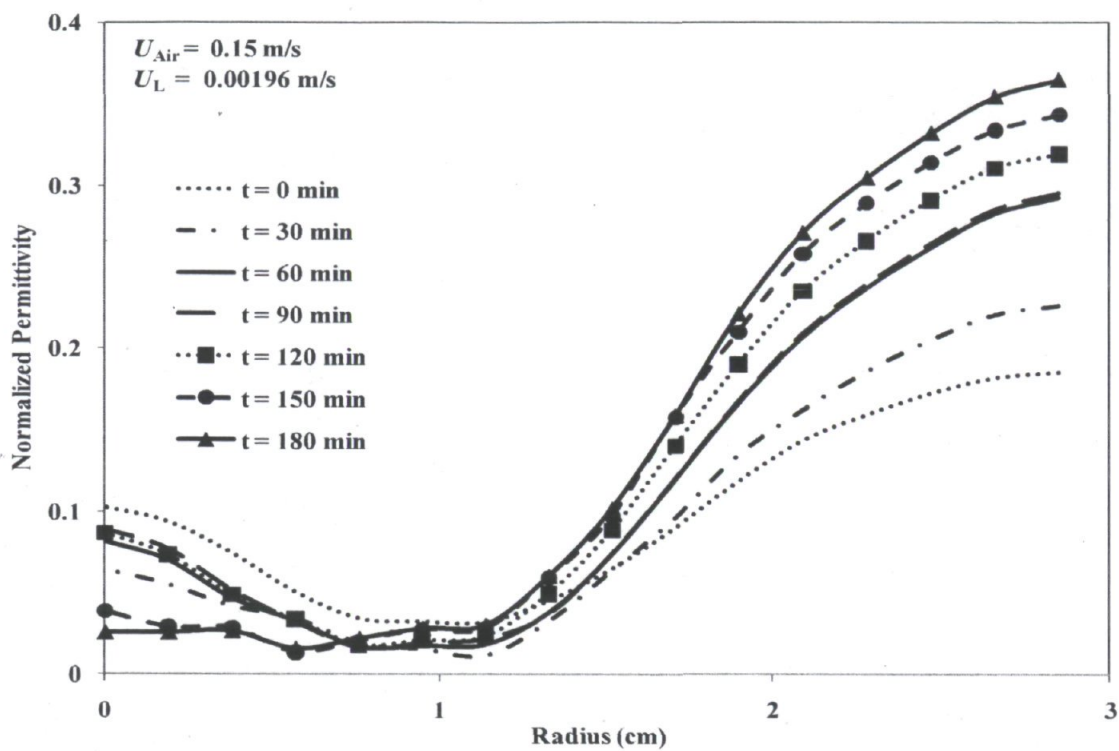


Figure 14 ECT normalized permittivity images during filtration in TBR at $U_{Air} = 0.15$ m/s and $U_L = 0.0013$ m/s at $t = 150$ min. (a) without upstream foam guards, (b) with 2 Al_2O_3 upstream foam guards, (c) with 1 Al_2O_3 upstream foam guard and (d) with 2 SiC upstream foam guards. Red = 100 %, blue = 0 %.

Fig. 14a shows ECT normalized permittivity image of TBR at 150 min during filtration. It shows higher deposition (red spot) in the bed center where bed permeability is lower. Figs. 14b,c show ECT normalized permittivity images of TBR during filtration with 1 and 2 Al_2O_3 upstream foams in separate experiments. These images show that presence of upstream foams has significant impact on normalized permittivity trend in TBR and there is significant drop in deposition inside TBR. Lesser deposition is observed at the center due to foam blockage as shown previously (Fig 12). Fig. 14d shows ECT normalized permittivity image for experiment carried out with 2 SiC foams as upstream guard in TBR. It reveals some drop in deposition as compared to filtration in TBR without upstream foams but this drop is not as significant as in the case of Al_2O_3 foams as upstream guards. The deposition pattern is similar to the deposition without the presence of foams.

Filtration experiment was carried out in a column packed with Al_2O_3 foams (bed height = 80 cm). ECT sensor was placed at the bed top. Fig. 15a shows normalized permittivity curves during filtration. Normalized permittivity increases along the radius of bed and at the center hardly any deposition has been experienced due to lesser suspension flux at the bed center which is visible in ECT images in Fig.15b. This is because of blockage of foam from center (Fig. 12). If this manufacturing drawback is removed alumina foams would work more efficiently as upstream guards because more surfaces will be utilized by the foams during two-phase flow to capture the fines from suspension stream. Fig. 15c shows a top view of Al_2O_3 foam after filtration which shows formation of deposition layer in annular shape at the top confirming the ECT images taken during experiment.



(a)

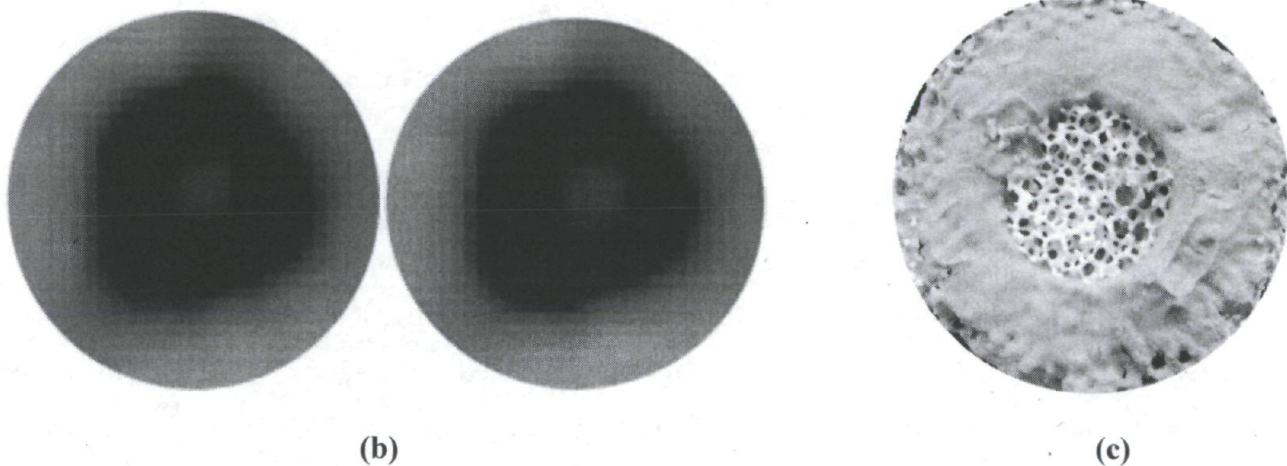


Figure 15 (a) Normalized permittivity along the radius of Al_2O_3 foams during filtration at $U_{Air} = 0.15 \text{ m/s}$ and $U_L = 0.00196 \text{ m/s}$ (b) ECT normalized permittivity images during filtration in Al_2O_3 foams at $t = 150 \text{ min}$ and 180 min ($U_{Air} = 0.15 \text{ m/s}$ and $U_L = 0.00196 \text{ m/s}$), red = 100 %, blue = 0 % (c) Top view of alumina foam (under distributor) right after filtration test.

Supporting Information

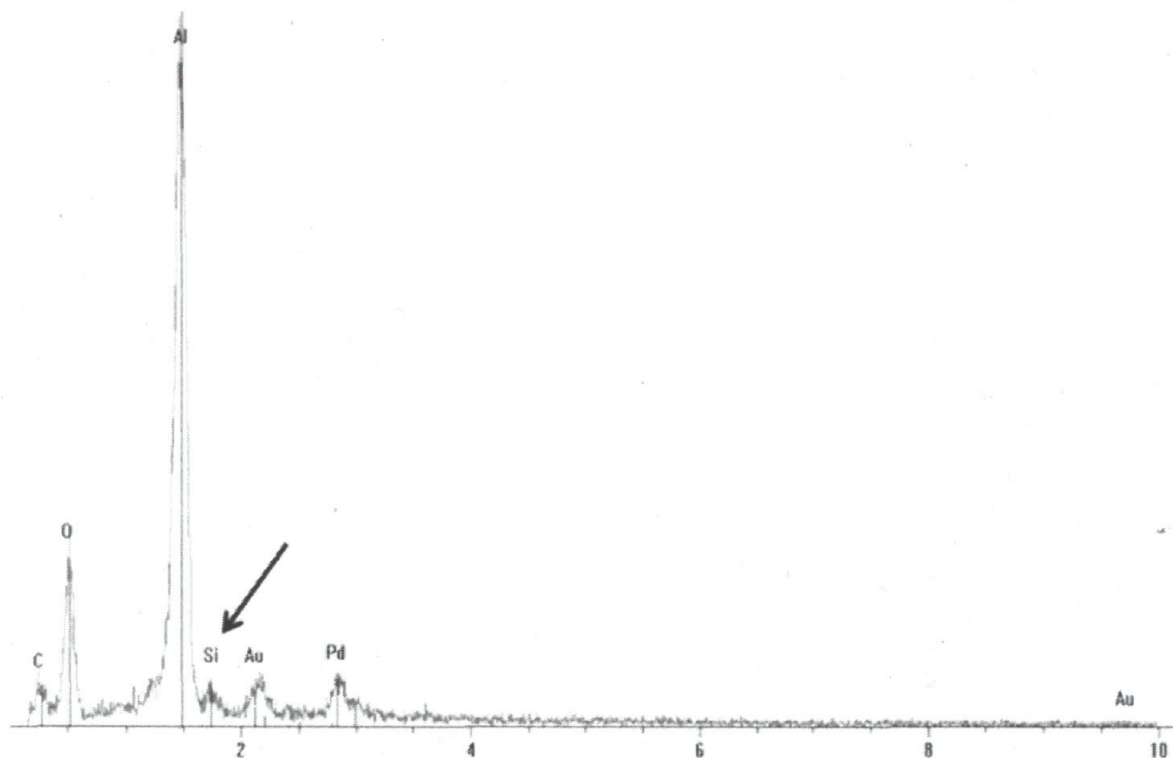


Figure SI 1 EDS analysis of catalyst after filtration experiments, shows presence of silica particles inside porous catalyst.

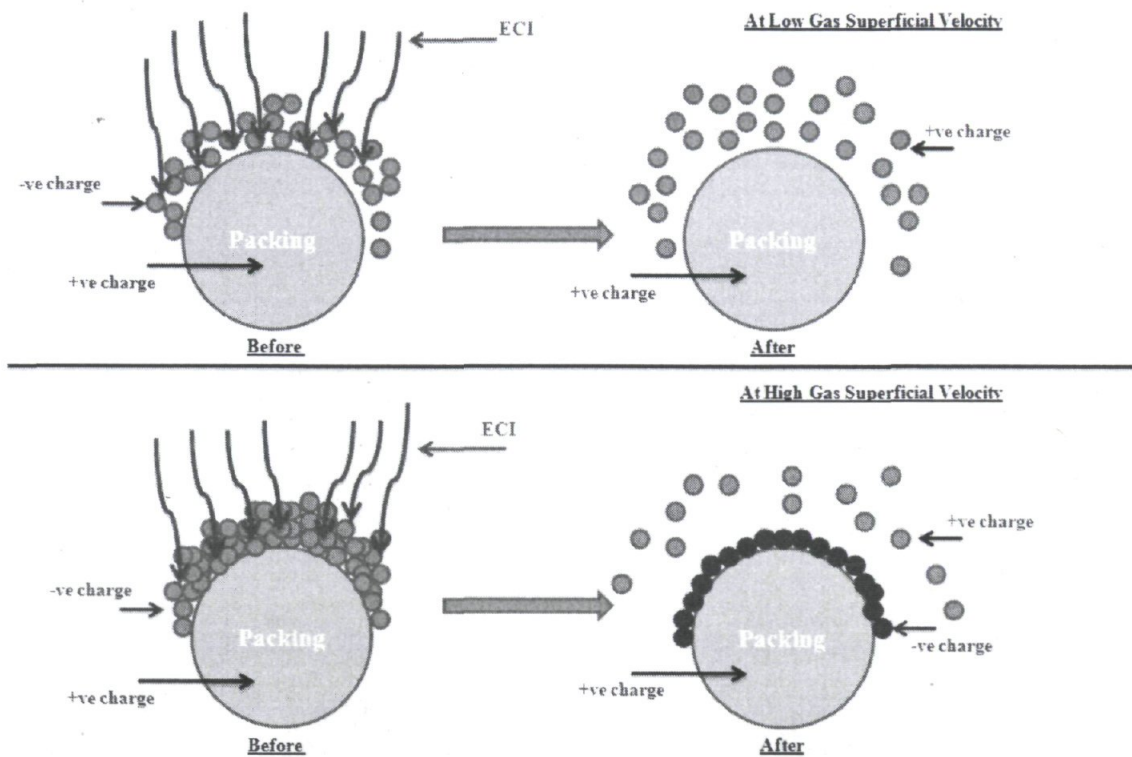


Figure SI 2 Before and after introduction of ECI during filtration at low and high superficial velocities, ECI impulsion access the entire layers prompting surface charge changes everywhere as alumina bed charges remain unaltered, repulsive forces between surfaces charged alike will prompt detachment which is more significant during filtration at low gas superficial velocity than high gas superficial velocity.

1.5 Conclusion

Today current reservoirs of unconventional heavy crude oil and bitumen have exceeded the known conventional crude oil resources. The application of TBRs in upgrading of oil sands and unconventional heavy crude bitumen is highly important. Deposition of fine solid particles in trickle bed reactor can cause server operating problems like increase in pressure drop and could also reduce the catalytic performance of bed. Experiments were carried out to investigate the effect of deposition on conversion of α -methylstyrene into cumene in TBR with/without filtration at room temperature and atmospheric pressure. Experimental results showed a drop in catalytic performance under filtration conditions. This drop in catalytic performance and activity is due to physical blockage of active sites because of deposition of fine particles on porous catalyst. Effect of compact and impact deposition on rate of conversion was investigated. It was observed that at same bed overall specific deposit achieved during single-pass at low and high gas superficial velocities, conversion is higher when deposition is less compact. Foam structures have been recently introduced to overcome some of the drawbacks packed bed has been facing. Their high porosity results in significant reduction of pressure drop per unit length even at high gas/liquid space velocity. Filtration experiments were conducted with alumina and SiC solid foams as upstream guards in TBR. Effect of upstream foam guards was investigated with help of electrical capacitance tomography to understand the structure of deposition inside TBR with/without foams. Significant reduction in pressure drop and deposition of fine particles were observed when these guards were placed upstream. It is revealed that alumina foams have more ability to capture fines as compared to SiC foams. If manufacturing techniques of alumina foams can be improved, as they were blocked from center, they can work more efficiently as upstream guards to capture the fine particles as more surface area will be available for liquid to be in contact with foams. This reduction in pressure drop and deposition inside catalytic bed can increase the catalytic performance and prolong the operational life of TBR.

ACKNOWLEDGMENT

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NOMENCLATURE

| | |
|----------------|--|
| $C_{T,IN,OUT}$ | finest concentration in the suspension (kg/m^3) |
| H | height of bed (cm) |
| P | pressure (Pa) |
| Q | volumetric flow rate (m^3/s) |
| t | time (s or h) |
| U_{Air} | air superficial velocity (m/s) |
| U_g | hydrogen superficial velocity (m/s) |
| U_L | liquid (clean/suspension) superficial velocity (m/s) |
| V_R | volume of reactor (m^3) |
| V_T | volume of tank (m^3) |

Greek Letters

| | |
|----------|--------------------------------------|
| σ | specific deposit (kg/m^3) |
|----------|--------------------------------------|

Abbreviations

| | |
|-----|-----------------------------------|
| ECI | Electrical Conductivity Improver |
| ECT | Electrical Capacitance Tomography |
| MP | Multi-Pass |
| SP | Single Pass |
| TBR | Trickle Bed Reactor |

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Chapter 3: Conclusion and Recommendations for Future Work

Today current reservoirs of unconventional heavy crude oil and bitumen have exceeded the known conventional crude oil resources. The application of TBRs in upgrading of oil sands and unconventional heavy crude bitumen is highly important. As Oil sands are a mixture of sand/clays, bitumen and water so some of solid fine particles (less than 20 μm) may enter hydrotreater after passing through all the prior filters and deposition of these fine particles in trickle bed reactor on catalyst can cause server operating problems like increase in pressure drop and could also reduce the catalytic performance of bed. Foam structures have been recently introduced to overcome some of the drawbacks packed bed has been facing. Their high porosity results in significant reduction of pressure drop per unit length even at high gas/liquid space velocity. Foams (SiC and AlO_3) were tested as upstream guards in Trickle bed reactor during experiments and their performance was investigated during filtration. It has been revealed that if these foams are going to be used as upstream guards it could help to minimize the deposition of fine particles which are managed to pass through the filters prior to hydrotreater and ultimately it will help to prolong the life of bed and improve chemical reaction which is important environmental point of view also because it will help to remove all those undesired components present inside hydrocarbons more efficiently which become source of pollution later.

As mentioned earlier not many articles are available in the literature addressing two-phase flow filtration in non-aqueous media. Effect of deposition on catalytic conversion and filtration with upstream foams as guard to investigate their effect on deposition of fine particles in Trickle Bed Reactor were studied in this work while several other parameters need to be investigated.

Liquid-solid mass transfer

Liquid-solid mass transfer could be affected by deposition of fine particles on surface of catalyst i-e it could be slowed down. Dissolution of solid particles (soluble in liquid phase) experiments could be performed to investigate this parameter. Dissolution of β -naphthol in kerosene method can be used as it is soluble in kerosene and spectrophotometer can be used to analyze the concentration of β -naphthol at outlet. β -naphthol particles can be prepared by following the approach proposed by Baussaron (Ph.D. thesis, 2005, Étude du mouillage partiel et du transfert de matière liquide-solide en réacteur à lit fixe arrosé, Institut National Polytechnique de Toulouse) and the packed bed can be filled with these spheres or with a mixture of alumina and β -naphthol. Height of the bed should be adjusted carefully to

prevent saturation concentration at reactor outlet and to extract the liquid-solid mass transfer coefficient.

Gas-liquid mass transfer

During two phase flow in trickle bed reactor, presence of fine particles inside liquid phase can offer resistance against dissolution of gas in liquid where fines accumulate along the gas-liquid interface. This parameter cannot be investigated by performing catalytic conversion experiment because of presence of fine particles on surface of catalyst. A proper way should be indentified to measure the concentration of gas dissolved in liquid at the outlet of the reactor to investigate the gas-liquid mass transfer coefficient.

Reaction with cyclic operation

Gas-liquid alternating cyclic operation strategy has been used in previous studies to investigate their effect on deposition and it proved to be efficient cleaning approach but this cyclic operation strategy has not been tested yet during chemical reaction to monitor their impact on conversion so this point should be investigated in future studies.

Reaction with electrical conductivity improver

Non-polar organic electrical conductivity improver modulation technique has been proved efficient in detachment of fine particles deposit on surface of catalyst but their effect on chemical reaction is still unknown which need to be verified.

Selectivity reaction

Selectivity and yield of chemical reaction can be affected by presence of deposit layer of fine particles on surface of catalyst as it has been experienced during conversion of α -methylstyrene to cumene with filtration. This effect cannot be interpreted straightforwardly. During selectivity reaction, intermediate product is formed before reaching to final product on catalyst surface. The selectivity can increase toward final reaction product if deposition layer on the surface of catalyst prevent the intermediate product to reach back to the liquid bulk. Catalytic conversion study of phenylacetylene to styrene and ethylbenzene with/without filtration would be interesting to investigate.

Gas/liquid limited condition for reaction

In industry during hydrotreating process, Hydrodesulphurization (HDS) reaction is carried out under liquid limited conditions because pressure inside reactor is high to increase the solubility of gas in liquid. During current research studies not adequate facilities were available in the lab to perform experiments at high pressure and temperature to reach liquid limited conditions. These factors should be studied in the detail to see their effect on deposition and chemical reaction due to their similarity to real operating conditions.

