



## Research article

## Deposition of fine particles of gas oil on hydrotreating catalyst: Impact of process parameters and filtration trends

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## ABSTRACT

When fine particles suspended in the gas oil feed come in contact with the hydrotreating catalyst at the reaction conditions, there is a change in the surface chemistry of the particles and they settle on the catalyst bed. The increase of the particle concentration in the catalyst bed leads to pressure drop in the reactor and eventually to catalyst deactivation. In this study, the impacts of process parameters such as temperature and pressure on particle deposition were studied. Also, the impact of particle size, reaction time and catalyst regeneration studies were conducted. For rationalization of the batch reactor set-up, used for hydrotreating, the catalyst was packed in a catalyst basket with a forced longitudinal feed flow through the packed catalyst bed in the basket. The spent catalyst was examined using various characterization techniques to understand the physical and chemical impacts of particle deposition on the hydrotreating catalyst. It was found that temperature significantly impacts particle deposition. Asphaltene coated kaolin has a preferential deposition on the reactor assembly and thus the overall bed deposition this case was less as compared to uncoated kaolin. When there was no catalyst packed in the basket, there was negligible bed deposition. Thus, it could be inferred that catalyst-fines interaction is chemical in nature.

## 1. Introduction

The process streams in the petroleum industry are hydrotreated in the packed catalytic columns to selectively remove heteroatoms by undergoing hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) [1]. These process streams, in addition to the heteroatoms, contain particles that remain entrained in the stream. The gas oil streams derived from Athabasca bitumen have sand or clay particles that surface adsorb organic layer called asphaltene [2]. Particles usually < 20 μm enter the hydrotreating unit with the process stream as the guard-bed filters are unable to retain these particles. The entrained particles settle on the catalyst bed causing gradual pressure drop in the hydrotreater and lead to premature catalyst deactivation and reactor shut-down [3]. The concentration of the particles entrained in the feed is as low as 100–200 ppm, yet the prolonged exposure of the catalyst bed to large quantities of feed leads to an increased accumulation of particles [4,5].

At hydrotreating conditions, the organic layer over the clay particles desorbs and this causes these clay particles to drop on the catalyst bed [6]. Hydrotreating barrels of oil eventually leads to the blockage of the

void spaces in the catalyst bed and results in ‘bed ripening’ where the catalyst bed gets completely clogged [7,8]. There are several approaches being considered to understand the reason behind the sudden pressure drop and it is found that the advent of pressure drop directly correlates to particle deposition as a function of time. It is reported that the nature of the particles impacts their interaction with the hydrotreating catalyst. HDO causes the formation of H<sub>2</sub>O and results in desorption of asphaltene from clay surface exposing the solid surface to more hydrophilic areas thus escalating the tendency of the particles to deposit on the catalyst [9].

There have been studies conducted to develop models for pressure-drop build-up and particle dynamics in the packed column [10,11]. Narayan et al. reported that a relative increase in pressure drop was observed at low Reynolds number due to the accumulation of particles in the voids and on the catalyst pellets [6]. When undisturbed, these particles settle covering the interstitial solids. However, when the feed flows through the catalyst pores, these particles remain entrained in the oil and deposit at the preferred accumulating sites [12].

The surface chemistry of the catalyst-fines interaction has also been studied [13]. The theories for the mechanism of particle deposition

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have been proposed which indicate that the particles have single layer, followed by double-layer and then multi-layer deposition. To enhance this kind of multi-layer deposition, a strong particle-particle interaction is required and this suggests an agglomerating nature of the clay particles [14,15]. It is understood that due to the removal of the organic coating on the clay particles, the steric repulsive forces that were inhibiting the particle-particle interaction are weakened [16]. Thus, the clay particles begin to agglomerate in the catalyst bed after the advent of particle deposition. However, the impact of process parameters has not been studied in the literature. There is a possible range of temperature (350–390 °C) and hydrogen partial pressure (1000–1500 psig) that can be used to hydrotreat the process stream, depending on the origin and nature of the stream [17]. Additionally, the quantitative and qualitative analyses of particle deposition along with catalyst activity have not been clearly reported in the available literature.

The objective of this work was to study the impact of process parameters on particle deposition with quantitative analysis of particle deposition and sulfur conversion of the feed. The reaction chemistry is reported to be predominantly controlled by the reaction conditions; wherein temperature is proposed to play the key role. Thus, the impact of temperature on particle deposition was of interest, especially due to the presence of asphaltene. Another process parameters studied was pressure and the impacts of particle size and reaction time were also studied to bring some further insight to this work. A few blank runs (without catalyst in the packed bed) were performed to check the selective deposition of particles on catalyst surface due to catalyst-particle interaction. The reactions were carried out in a batch reactor with light gas oil as the feed and asphaltene coated kaolin as model fines.

## 2. Experimental set-up

### 2.1. Materials

Tri-lobed gamma alumina support was supplied by Sasol, Hamburg, Germany. 3 mm glass beads were supplied by Fisher Scientific, Edmonton, Canada. Nickel nitrate hexa-hydrate, ammonium heptamolybdate, amorphous kaolin, butanethiol and hexane were purchased from Sigma Aldrich, Edmonton, Canada. Bitumen and LGO feed was provided by Syncrude Research Centre, Edmonton, Canada. 0.22 μm membrane filters were purchased from Millipore, Toronto, Canada.

### 2.2. Catalyst preparation

The sequential incipient wet impregnation method was employed to prepare the catalyst. Molybdenum, 13 wt% from the precursor  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  was impregnated on the support. After impregnating, the support was left to dry for 6 h at 100 °C and then calcined at 550 °C for 5 h. Followed by molybdenum, 2.5 wt% nickel was impregnated on the support. Nickel nitrate hexahydrate was used as nickel precursor. After impregnating nickel, the support was dried at 100 °C for 6 h and then calcined at 550 °C for 5 h to obtain  $\text{NiMo}/\gamma\text{Al}_2\text{O}_3$  catalyst.

### 2.3. Experimental setup

The hydrotreating experiments were performed in a batch reactor installed with a catalyst basket. The purpose of using a batch system was to accelerate the rate of particle deposition on the catalyst bed which is comparatively very slow in case of trickle beds. To keep the catalyst particles undisturbed during the feed mixing, the catalyst bed was packed in a catalyst basket that sat undisturbed in the reactor vessel. The impeller was installed to force the feed flow upwards so that the feed could drop through the catalyst bed as in the trickle bed set-up instead of having a radial flow that is usual for batch reactors (Fig. 1). The mesh size of the screens of catalyst basket were selected to allow the feed and particles to pass through but hold the glass bead, SiC and

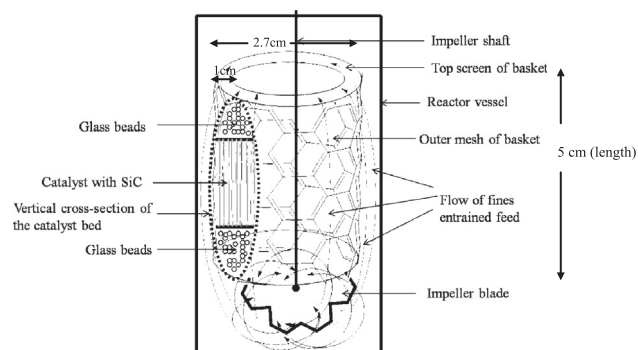


Fig. 1. Schematic representation of feed flow with the catalyst basket in static mode.

catalyst packed. For each hydrotreating run, 1 g of catalyst was packed in the catalyst basket. Two 450 ml reactor vessels were used for sulfidation and hydrotreating each. Constant flow of hydrogen was maintained with the help of back-pressure regulator and after the reaction completion, the reactor was depressurized by venting the gasses through the NaOH scrubber.

### 2.4. Synthesis of model fine particles

Model fines were synthesized in the laboratory. Asphaltene was extracted from Athabasca bitumen and the procedure for the extraction of Asphaltene is explained below in this section. Commercial kaolin of two different sizes was coated with asphaltene to prepare two batches of asphaltene coated kaolin of varying sizes. The size and carbon content of asphaltene, kaolin and model fines used are reported in Table 1. It is clear from Table 1 that pristine kaolin contains negligible carbon; however after asphaltene coating the carbon content of the coated kaolin increases. Also, there is an increase in the size of asphaltene coated kaolin as compared to pristine kaolin. This suggests that the synthesized model particles were asphaltene coated kaolin.

The synthesis of asphaltene coated kaolin was divided into two major steps-

- Extraction of asphaltene from bitumen  
To extract asphaltene from bitumen, soxhlet extraction process was used. The first step was to dissolve asphaltenes in toluene. Toluene was added to bitumen in a beaker maintaining 40:1 ratio. The mixture was stirred at room temperature till the highly viscous bitumen was completely mixed with the solvent (toluene). The mixture was then centrifuged at 3000 rpm for 1 h. The solvent in the supernatant was collected by drying the supernatant in a rotary evaporator. The thick viscous mass collected in the flask was dried at 70 °C overnight to remove volatiles. The remaining mass was then transferred to a thimble and the collected mass was washed with n-heptane to dissolve any remaining maltenes in the collected mass. Asphaltene is heptanes-insoluble and hence the mass left in the thimble after heptanes washing was asphaltene. The collected asphaltenes were vacuum dried at 70 °C overnight.
- Preparing Asphaltene coated kaolin (model fine particles)  
For the synthesis of fine particles, 1:5 ratio of asphaltene to kaolin

Table 1  
CHNS and particle size analysis of kaolin, asphaltene and prepared fines.

Sample name	Carbon content (wt%)	Size range (μm)
Kaolin 1	00.13	6–7
Kaolin 2	00.08	2–3
Asphaltene	80.00	–
Fines from kaolin 1	3	9–11
Fines from kaolin 2	5	4–6

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