



Characterization of a continuous micro-scale pilot unit for petroleum residue hydroconversion with dispersed catalysts: Hydrodynamics and performances in once-through and recycling mode

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HIGHLIGHTS

- Heavy oil hydroconversion was studied in a continuous unit with a dispersed catalyst.
- Hydrodynamic behavior was studied in a cold mock-up.
- Once-through and recycle mode operations were compared.

ARTICLE INFO

Article history:

Received 10 January 2014

Received in revised form 25 April 2014

Accepted 7 May 2014

Available online 14 May 2014

Keywords:

Residue hydroconversion

Dispersed catalyst

Continuous micro-pilot unit

Recycling

Cold mock-up

Hydrodynamics

ABSTRACT

A continuous micro-pilot unit has been designed to convert petroleum residues with dispersed catalysts. Once-through and recycling modes can be operated. Several operating conditions (residence times and temperatures) have been investigated using the molybdenum naphthenate as catalyst precursor (600 ppm). The micro-pilot hydrodynamics has been characterized via a cold mockup by Residence Time Distribution. Whatever the mode used, the conversion, product yields and average molecular weights depends only on residence time and temperature.

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1. Introduction

Demand for high value petroleum products such as distillates is still increasing. Therefore, heavy oil conversion has become a challenging task for refiners. The heavy oil fractions are complex feedstocks. In fact, they contain large molecules such as heteroatoms containing compounds (nickel and vanadium or sulfur and nitrogen) and asphaltenes. These last could precipitate to form coke in severe operating conditions thus limiting conversion level due to sediment formation [1]. Several technologies have been developed over the years for residual oil upgrading; they can be either non catalytic or catalytic residue processes using fixed or ebullated beds. In the absence of catalyst, thermal reactions take place

producing a large quantity of coke while the catalytic processes operating under high hydrogen pressure allowing high selectivity towards liquid products. These catalytic processes can be performed under severe operating conditions to provide higher liquid yields while being selective towards the gasoil cut without forming coke [2,3]. Ni–Mo or Ni–W sulfide catalysts supported on alumina are usually used. However, as heavy oil fractions contain high amounts of contaminants such as Ni and V, the pore entrances of the catalyst may become blocked by metal and coke deposition, leading to rapid catalyst deactivation [4–6].

These shortcomings have led to the development of the so-called slurry phase hydroconversion technology. These processes are operated in the presence of dispersed catalysts with sub-micronic particle size and allow conversion levels above 90% of the residue fraction [7]. The catalyst allows hydrogen activation, facilitating hydrotreating reactions and limiting the thermal

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Nomenclature

Parameter	Signification (unit)	P	power dissipated from the agitation ($\text{kg m}^2 \text{s}^{-3}$)
AR	atmospheric residue	PFR	plug flow reactor
C	volumetric tracer concentration	PMA	phosphomolybdic acid
C_{ali}	aliphatic carbon determined by NMR analysis (%)	PS	polystyrene
C_{aro}	aromatic carbon determined by NMR analysis (%)	Q_v^{liq}	volumetric flow rate of the liquid ($\text{cm}^3 \text{min}^{-1}$)
C_{sat}	saturated carbon determined by NMR analysis (%)	Q_v^{gas}	volumetric flow rate of the gas ($\text{cm}^3 \text{min}^{-1}$)
CH_{aro}	aromatic C–H group determined by NMR analysis (%)	RES	cut corresponding to the boiling point range of 510 °C+
CH_{ali}	aliphatic C–H group determined by NMR analysis (%)	Re	Reynold's number
C_{RES}	residue conversion (wt%)	S	sensitivity (Jacobian)
CSTR	continuous stirred tank reactor	S_{N-k}	student variable where N is the observation number and k is the parameter number
D	hydraulic diameter of the pipe (m)	THF	tetrahydrofuran
d	diameter of the stirrer (m)	v^{liq}	mean velocity of the fluid
$E(t)$	Residence Time Distribution	VGO	cut corresponding to the boiling point range of 350–510 °C
Feed	mixture of AR + LCO + catalytic precursor	T	temperature (°C)
Fr	Froude number	V	volume (cm^3)
$F_{j,1}$	mass flow rate of cut j at point 1 ($j = \text{RES, VGO, GO, NAPH, GAS}$) (g min^{-1})	V_R	micro pilot unit reactor volume (cm^3)
$F_{j,2}$	mass flow rate of cut j at point 2 ($j = \text{RES, VGO, GO, NAPH, GAS}$) (g min^{-1})	V_{11}	variance $V_{11} = (S^T S)^{-1}$
$F_{j,2'}$	mass flow rate of cut j at point 2' ($j = \text{RES, VGO, GO, NAPH, GAS}$) (g min^{-1})	Δ	sum of the squares of the difference between experimental and simulated data points
g	gravitational acceleration (m s^{-2})	ε	gas holdup (vol%)
GAS	cut corresponding to all non condensable gases except hydrogen	μ	dynamic viscosity ($\text{m}^2 \text{s}^{-1}$)
GO	cut corresponding to the boiling point range of 200–350 °C	ρ	density of the fluid (kg m^{-3})
L^{tube}	length of the tubing (m)	σ	standard deviation
LCO	light cycle oil	τ	average residence time (h)
M_w	molar mass in polystyrene equivalents (g mol^{-1})	$\hat{\tau}$	estimation of τ_{CSTR} (s)
N	stirring speed (s^{-1})	τ_{CSTR}	residence time of a CSTR (s)
N_p	Power number	τ_{PFR}	residence time of a plug flow reactor (s)
NAPH	cut corresponding to the boiling point range of 40–200 °C	ζ	adimensional axial coordinate of a PFR

reactions. Therefore, coke formation is reduced and the hydrotreatment of large molecules is no longer limited by pore size, as for processes using a supported catalyst. The catalytically active phase is more accessible, consequently, the operating conditions may be more severe and the yield of desired products is increased. In comparison with classical processes like fixed beds, the catalyst of the slurry process remains in the heavy fraction of the products and is lost if recycling is not considered. Consequently, the design of a process including a continuous recycling is preferred.

Several studies have been performed in order to understand and optimize catalysts and process. Most of them have been conducted in batch reactors [8]. This type of reactor avoids plugging problems related to coke formation. Several catalyst precursors and their formulation, mainly with metals from group IV and V have been investigated [9–11]. Molybdenum is the most studied and has been used in different forms such as a naphthenate, acetylacetonate, ammonium heptamolybdate or chloride [9,12,13]. These molybdenum precursors were also investigated with an additive such as phosphorus [14] or promoters such as nickel or cobalt [10,11]. The influence of the operating conditions such as catalyst concentration, temperature, and pressure has been studied in batch reactor experiments [10,13,15]. Batch reactors have also been used to study the reaction kinetics and to propose reaction schemes based on those given for supported catalysts [15,16].

As some processes require the recycling of the in situ generated catalysts, batch reactors have also been employed to simulate this operating mode by reusing the solid-coke catalyst recovered from the reactor in subsequent experiments [17–20].

Publications concerning continuous flow reactors are scarce and performed in the once-through mode. They mainly concern the comparison of different catalysts such as limonite [21], Ni, Mo, Fe-based water soluble precursors [22–24] or the development of the kinetic models [25,26]. Recycling in the continuous mode has only been performed by Bellussi et al. [27] with bi-functional catalysts (MoS_2 and zeolite) but the role of recycling mode was not investigated.

In the present work, we report on the hydrodynamic characterization of a micro-pilot unit and the conversion of an atmospheric residue (AR) in a range of intermediate conversion levels for different operation modes. We investigate the role of the recycling in a continuous micro-pilot unit and its impact on the catalytic performance and its deactivation. The total volume of this micro-pilot being 100 cm^3 , the hydrodynamic behavior has been characterized via a cold mock-up and a Residence Time Distribution (RTD) study, taking into account the size of each element of the micro-pilot unit.

2. Materials and methods

2.1. Feedstock and catalyst

The atmospheric residue (AR) used for hydroconversion experiments was provided by TOTAL. Its average viscosity at 100 °C was 28.9 cSt. It contained 2.8 wt% of sulfur, 0.2 wt% of nitrogen and 2.1 wt% of asphaltene. The catalyst precursor was a commercial molybdenum naphthenate from Shepherd Chemical Company

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