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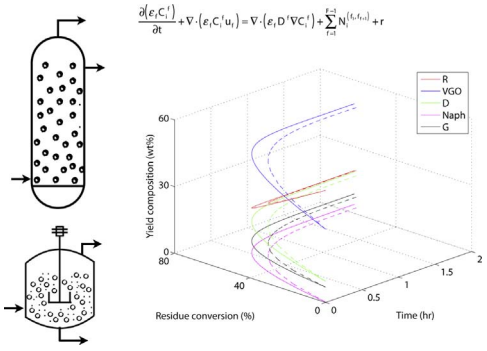
Full Length Article

Modeling of CSTR and SPR small-scale isothermal reactors for heavy oil hydrocracking and hydrotreating

Cristian J. Calderón[a], Jorge Ancheyta[b,*]

[a] Facultad de Química, UNAM, Ciudad Universitaria, Ciudad de México 04510, Mexico
[b] Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte152, Col. San Bartolo Atepehuacan, Ciudad de México 07730, Mexico

GRAPHICAL ABSTRACT



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ABSTRACT

The dynamic modeling and simulation of a continuous slurry phase reactor for catalytic hydrocracking and hydrotreating of an atmospheric residue (312 °C+) are reported. The reactor model is based on an axial dispersion. The hydrocracking kinetic model takes into account a five-lump model previously reported in the literature. The hydrotreating reactions simulated are: hydrodesulfurization (described by Langmuir–Hinshelwood kinetics), hydrodenitrogenation (for basic and non-basic nitrogen), hydrodeasphaltenization and hydro Conradson carbon removal (modeled with power-law approach). All the intrinsic kinetic parameters and correlations were taken from the literature. The performance for the slurry-phase reactor was compared with a continuous stirred tank reactor. Dynamic simulations and steady-state predictions agreed with the expected behavior of the heavy fractions and impurities hydroprocesing.

1. Introduction

Hydrocracking (HDC) is one of the most important technologies in oil refining. It consists of disintegrating heavy cuts with high molecular weight into lighter with low molecular weight fractions. This operation is carried out in multiphase reactors where the solid phase is the catalyst, usually sulfide of cobalt, molybdenum, or nickel supported on alumina or silica-alumina, the gas phase is mainly composed of hydrogen and the liquid phase is the hydrocarbon. There are different types of reactors, such as fixed, moving, and ebullated bed, however these reactors may face some complications due to high impurities content of residue feeds, and excessive hydrocracking of heavy fractions that leads to coke formation and metal deposition, which eventually deposit on the catalyst surface and result in catalyst deactivation [1].

* Corresponding author.
E-mail address: jancheyt@imp.mx (J. Ancheyta).

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Nomenclature

Symbols

API	API gravity
Asph	asphaltenes
BN	basic nitrogen
D	distillates
D_a	axial dispersion coefficient, m^2/hr
G	gases
HDC	hydrocracking reaction
HDT	hydrotreating reaction
i	Refering to *i* component.
k_{CAsph}	catalytic kinetic parameter for hydrodesasphaltenization reaction, $wt\%^{-0.503}hr^{-1}$
k_{CBN}	catalytic kinetic parameter for hydrodenitrogenation reaction of basic nitrogen, $ppm^{-0.792}hr^{-1}$
k_{CNBN}	catalytic kinetic parameter for hydrodenitrogenation reaction of non-basic nitrogen, $ppm^{-1.154}hr^{-1}$
k_{CS}	catalytic kinetic parameter for hydrodesulfurization reaction, $wt\%^{-0.503}hr^{-1}$
k_D	deactivation parameter, hr^{-1}
k_{TAsph}	thermal kinetic parameter for hydrodesasphaltenization reaction, $wt\%^{0.795}hr^{-1}$
k_{TBN}	thermal kinetic parameter for hydrodenitrogenation reaction of non-basic nitrogen, $ppm^{0.137}hr^{-1}$
k_{TNBN}	thermal kinetic parameter for hydrodenitrogenation reaction of non-basic nitrogen, $ppm^{0.137}hr^{-1}$
k_{TS}	thermal kinetic parameter for hydrodesulfurization reaction, $wt\%^{0.062}hr^{-1}$
k_1	intrinsic kinetic parameter for residue hydrogracking to vacuum gas oil, $g_T^n g_R^{-1} g_{Cat}^{-1} hr^{-1}$
k_2	intrinsic kinetic parameter for residue hydrogracking to distillates, $g_T^n g_R^{-1} g_{Cat}^{-1} hr^{-1}$
k_3	intrinsic kinetic parameter for residue hydrogracking to naphtha, $g_T^n g_R^{-1} g_{Cat}^{-1} hr^{-1}$
k_4	intrinsic kinetic parameter for residue hydrogracking to gases, $g_T^n g_R^{-1} g_{Cat}^{-1} hr^{-1}$
k_5	intrinsic kinetic parameter for vacuum gas oil hydrogracking to distillates, $g_T^n g_{Cat}^{-1} hr^{-1}$
k_6	intrinsic kinetic parameter for vacuum gas oil hydrogracking to naphtha, $g_T^n g_{Cat}^{-1} hr^{-1}$
k_7	intrinsic kinetic parameter for vacuum gas oil hydrogracking to gases, $g_T^n g_{Cat}^{-1} hr^{-1}$
k_8	intrinsic kinetic parameter for distillates hydrogracking to naphtha, $g_T^n g_{Cat}^{-1} hr^{-1}$
k_9	intrinsic kinetic parameter for distillates hydrogracking to gases, $g_T^n g_{Cat}^{-1} hr^{-1}$
k_{10}	intrinsic kinetic parameter for naphtha hydrogracking to gases $g_T^n g_{Cat}^{-1} hr^{-1}$
L	reactor length, m
m_T	total mass composition, g_T
Naph	naphthenes
NBN	non basic nitrogen
P	pressure, MPa
R	residue
S	sulfur
SG	specific gravity at 15.6 °C
t	time, hr
t_f	Final time, hr
T	temperature, K
u	feed velocity, m/hr
V	volume, m^3
VGO	vacuum gas oil
W_P	amount of catalyst in the feed, g
x_i	content of *i* component in the feed, g_i/g_T, ppm
x_i^0	initial content of *i* component, g_i/g_T, ppm
Z	reactor position, m

Greek symbols

η	Effectiveness factor
ν_i	Stechiometric coefficient of *i* component
φ	Function of catalyst deactivation

Also, these reactors experience high pressure drop of the bed which makes difficult to maintain a normal operation, therefore shut-down is more frequent due to short catalyst life and unstable operation of the reactor [2].

To address the disadvantages in HDC in conventional technologies, slurry-phase hydrocracking processes have been developed. This technology consists of mixing the oil feed, hydrogen, and dispersed catalysts together going through the reactor. It has the same processing as thermocracking but also reduces coking due to the presence of hydrogen and catalyst that promote hydrogenation reactions [3]. The catalyst also acts as a support for the low amount of coke that could be formed, and due to the catalyst leaves the reactor continuously this effect has no greater relevance in the operation. Depending on the oil to be treated, the catalysts are designed for the removal of impurities such as sulfur, nitrogen, metals and asphaltenes, even for the saturation of aromatics and olefins. All these reactions occur simultaneously and are known as hydrotreating reactions (HDT).

While slurry-phase reactors (SPR) for hydrocracking of heavy oil are a promising technology, plants at a commercial scale have not been developed or are still in the design stage due to high catalyst cost and elevated operating conditions necessary to achieve the conversion of the heaviest fractions of the feed [4]. In addition, SPR technology has some major disadvantages compared with fixed, moving, or ebullated bed reactors, such as the difficult separation of catalyst and the liquid product, uncertain scale-up, catalyst sedimentation and agglomeration, as well as the hard understanding of reaction kinetics and flow patterns [5].

Recent investigations concerning to kinetic models for hydrocracking in slurry-phase have been reviewed [4]. Due to heavy oil consists of a large amount of components, different approximations are used to represent hydrocracking reactions, being the most common the lumping techniques. The method consists of lumping various compounds in a few pseudocompounds that differ by boiling temperature range. This approximation is easy to implement in a reactor model because it reduces the number of kinetic equations and parameters to be estimated. On the other hand it is known that as long as the reaction rate coefficients have been obtained under kinetic regime, the kinetic model can be implemented in the reactor model independently if those parameters were obtained in a different type of reactor.

Moreover, the literature concerning mathematical modeling of hydrocracking in SPR's is scarce, as shown in a previous review work [5]. Most of the reports are based on computational fluid dynamics models (CFD) formulated in steady-state and focused on the performance of the hydrodynamic variables inside the reactor and not on residue conversion [6–10]. It should be pointed out that due to the difficulty for obtaining proper information, all those reactor models were validated with air–water systems. On the other hand, there are recent modeling reports dealing with hydrocracking in industrial and pilot plant units [11,12]. However, such models are based on ideal plug-flow patterns in steady-state.

Recent models for SPR's have been published. Those reactor models were formulated for different reacting systems, such as Fischer–Tropsch synthesis, methanol synthesis, dimethyl ether synthesis, and diesel