Kinetic analysis of vacuum residue hydrocracking in early reaction stages

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HIGHLIGHTS

- NiMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$–Cr were tested in vacuum residue hydrocracking reactions.
- Ten lumped kinetic models with increasing complexity were developed.
- The reversibility of the reactions, including coke formation, was taken into account.
- Reaction pathways at different temperatures were described.
- The most complex model accurately described the systems at all temperatures.

ARTICLE INFO

ABSTRACT

In this work, a lumped kinetic model for the hydrocracking of vacuum residue (VR) from Maya crude oil was developed. A preliminary kinetic analysis based on the conversion of VR was performed. Next, ten models with increasing level of complexity were proposed and solved sequentially using Matlab® software. All models included four lumps: products with boiling point >450 °C (L+), products with boiling point <450 °C (L−), gas and coke. Kinetic parameters were estimated from the experimental data obtained in a microbomb batch reactor at three temperatures (400, 425 and 450 °C) and four holding times (10, 30, 60 and 90 min). Two catalysts, NiMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$–Cr (alumina doped with chromium), were tested. Kinetic results showed that gas was mainly produced from the decomposition of L− at low temperatures, whereas at 450 °C gas is predominantly formed from cracking of L+. Moreover, coke was found to be exclusively produced from L+ at all temperatures. In general, NiMo/Al$_2$O$_3$ gave rise to higher yields of L− than NiMo/Al$_2$O$_3$-Cr. Nevertheless, NiMo/Al$_2$O$_3$-Cr was able to retain greater activity at higher temperatures.

1. Introduction

Heavy oils are becoming increasingly important due to the decrease in conventional oils and the development of novel technologies for extraction and processing of heavy feeds. Thus, heavy oil production is expected to reach a peak production of 12.3 mbd in the year 2020 [1]. Hydrocracking is generally considered as one of the most efficient technologies for converting bottom of the barrel fractions into lighter products of higher value. This process involves the use of bi-functional catalysts at temperatures around 370–450 °C with relative high hydrogen pressure of the order of 100–140 atm [2]. The development of active, metal-tolerant and coke-resistant hydrocracking catalysts has been the subject of numerous studies. Metal combinations of Mo or W promoted by either Ni or Co providing the hydrogenation function are most widely used. These metals are usually dispersed onto different supports such as γ-alumina, zeolites, silica and silica–aluminates [3], which provide the acidic catalyst function.

The development of robust kinetic models of heavy oil hydrocracking is not straightforward due to the complexity of these hydrocarbon feedstocks, the analysis of its components as well as the complex reaction networks [4]. Hydrocracking of heavy oils involves an extremely large number of hydrocarbon species related through numerous reactions. In particular, asphaltenes, the solubility class containing the most complex structures in heavy oils, cover a broad range of compounds. Large asphaltene molecules are commonly rich in polyaromatic hydrocarbons (PAH) [5]. Additionally, several other hydrocarbon types can be identified in heavy oils, such as saturated, branched and metalloporphyrins, among many others [6]. Different approaches have been reported for kinetic modelling of heavy oil hydrocracking, although the most commonly used method is the lumping technique [7–11]. Due to the complex nature of heavy oil feedstocks, considering each

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Nomenclature

VR	vacuum residue
L+	Products with boiling point >450 °C
L−	Products with boiling point <450 °C
G	Gas
C	Coke
y_{L+}	yield of products with boiling point >450 °C
y_{L-}	yield of products with boiling point <450 °C
y_G	yield of gas
y_C	yield of coke
r_{L+}	reaction rate of products with boiling point >450 °C (min^{-1})
r_{L-}	reaction rate of products with boiling point <450 °C (min^{-1})
r_G	reaction rate of gas (min^{-1})
r_C	reaction rate of coke (min^{-1})
k_1	first-order rate constant for the reaction of products >450 °C to products <450 °C (min^{-1})
k_2	first-order rate constant for the reaction of products <450 °C to gas (min^{-1})

k_3	first-order rate constant for the reaction of products >450 °C to coke (min^{-1})
k_4	first-order rate constant for the reaction of coke to products >450 °C (min^{-1})
k_5	first-order rate constant for the reaction of products >450 °C to gas (min^{-1})
k_6	first-order rate constant for the reaction of coke to gas (min^{-1})
k_7	first-order rate constant for the reaction of products <450 °C to products >450 °C (min^{-1})
k_8	first-order rate constant for the reaction of products <450 °C to coke (min^{-1})
k_9	first-order rate constant for the reaction of coke to products <450 °C (min^{-1})
E_a	activation energy (J/mol)
X	VR conversion
m_{VR}	weight of the VR (g)
m_{L+}	weight of products >450 °C (g)

compound independently in the kinetic model is not feasible. The lumping technique consists of grouping species present in the process based on shared characteristics, such as boiling point, functional group, chain length, molecular weight, polarisability or polarity [8]. The discrete lumping method is a traditional approach that groups species by boiling points covering the whole range in the reaction system; the groups are then linked to one another through reaction pathways. This approach presents the advantage of limiting the number of reactions and reducing the number of estimated parameters in the study. This method has been used extensively for hydrotreating and hydrocracking reactions [8,10,12,13].

In this work, hydrocracking kinetics have been studied at short reaction intervals. In the kinetic model developed, coke was considered a by-product of reaction. It is of great importance to consider coke as product as it has been shown that coke is involved in reversible reactions at short and even relatively long reaction time intervals [14]. Coke is mainly formed from the polymerization of PAH structures on the catalysts surface. Additionally, coke is known to continuously exchange material with the liquid phase even when no net build-up of coke is observed [15].

The aim of this work is to perform a kinetic analysis of the hydrocracking of a vacuum residue (VR) over mesoporous alumina supported NiMo catalysts at short reaction times. Experimental data were obtained from runs carried out in a microbomb batch reactor at three temperatures (400, 425 and 450 °C) and four holding times (10, 30, 60 and 90 min), both using NiMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$–Cr (alumina doped with chromium) catalysts. A preliminary approach in the kinetic analysis was performed solely taking into account the conversion of VR to products. Afterwards, ten models based on the lumping technique by boiling point presenting an increasing level of complexity were proposed and solved sequentially via Matlab® software.

2. Experimental

2.1. Materials

A sample of VR obtained from Maya crude oil, a heavy oil with a large heteroatom content, was employed as feedstock. The VR,

which is solid at ambient temperature, was used as received without dilution. Table 1 shows the main physicochemical properties of the VR. The VR presents particularly high heteroatom content, high viscosity and coke forming tendency reported as Conradson carbon number. Moreover, the Maya VR is challenging to upgrade compared to other residua since the relative reactivity of asphaltenes is very low [16].

Two catalysts, NiMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$–Cr (alumina doped with chromium), were employed in all experiments. An alumina support with large surface area and pore volume was synthesized by following a procedure available in the literature [17]. A mixture of ethanol and propanol were used to dissolve aluminum isopropoxide. Then a non-ionic surfactant (Pluronic F127) was added with water to create an emulsion. The gel was aged overnight at room temperature and then filtered to obtain a wet paste which was dried further and calcined at 550 °C for 8 h. The molar ratios of the components in reference to aluminum isopropoxide were 8, 6, 0.01 and 20 for ethanol, propanol, F127 and water, respectively. The alumina doped with chromium was synthesized by using an aqueous solution containing Cr(NO$_3$)$_3$·9H$_2$O instead of water. The chromium salt concentration was calculated to 6% wt of Cr$_2$O$_3$ in the calcined alumina. The metallic catalysts were prepared by the incipient wetness impregnation method with successive impregnation of the precursor salts, (NH$_4$)$_2$MoS$_4$ and Ni(NO$_3$)$_2$ with intermediate drying steps at 80 °C for 12 h. The Mo and Ni salts were diluted with diethylenetriamine (DETA) and water in a 10:1 vol/vol ratio and water, respectively. The dilution calculations

Table 1
Physicochemical properties of the vacuum residue used as feedstock.

Boiling point interval (°C)	540+
Specific gravity at 15 °C	1.08
°API gravity	−0.34
Viscosity at 100 °C (cSt)	265,546
Sulfur content (wt.%)	7.02
Conradson carbon (wt.%)	25.54
Asphaltenes (wt.%)	33.63[a]
Ni (ppm w/w)	102
V (ppm w/w)	169

[a] Determined with same method as reaction products described in Section 2.2.