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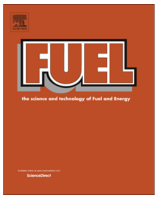

Full Length Article

A viscosity-conversion model for thermal cracking of heavy oils

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ABSTRACT

Thermal cracking processes such as visbreaking are used in the petroleum industry to reduce the viscosity of heavy feedstocks, such as atmospheric and vacuum residues, without forming coke or unstable asphaltenes. Thermal cracking offers a potential method to reduce the viscosity of heavy oils and bitumen, enabling their pipeline transportation with less solvent addition. Viscosity is the most important property for transportation of crude oils, but this property also has a highly non-linear dependence on temperature and composition. In this work, we used a lumped-kinetic model, based on boiling point pseudo-components, coupled with a fluid property model, to correlate the viscosity of two heavy oils subjected to thermal cracking reactions at different severities, and assess the impact of the chemical transformations on the behavior of the heaviest fraction. The properties of these pseudo-components were estimated by validated correlations, and tuned with experimental values. By assuming that after the reactions these properties remained invariable in each boiling point pseudo-component, we could estimate the viscosity of the liquid products from the recombination of these individual properties using mixing rules available in literature. The results indicated that the vacuum residue fractions (>524 °C) undergo chemical transformations that alter their fluid properties. By using adjusting factors dependant on conversion, we were able to make estimations of viscosities at different temperatures with absolute average deviations lower than 25%.

1. Introduction

Mild thermal cracking is commonly used in refineries to reduce the viscosity of fuel oils [1]. Due to widespread interest in pipeline transportation of heavy crude oils without the addition of diluent, thermal cracking processes such as visbreaking have gained increased attention for potential use in the field [2]. These processes offer low energy consumption, simplicity, and low-cost, but the level of conversion is limited by the increased instability of the asphaltene fraction and by fouling of equipment [3]. In order to achieve the target viscosities, combinations of thermal cracking, deasphalting, and addition of diluents have been proposed. Visbreaking is a well-established refinery process, and a number of kinetic models and methods for reactor modeling have been developed, as reviewed by Joshi et al [3]. The commercial reactors are not isothermal, so the models commonly use the severity of reaction to relate conversion to time at a fixed reference temperature. The bigger challenge is to couple the conversion model with a model for viscosity, so that the properties of the product blend can be defined as a function of conversion of the vacuum residue. Dente and coworkers [4,5] proposed a comprehensive model for reaction kinetics and product properties, with detailed modeling of elementary reaction steps for free-radical chain reactions. This approach is rigorous, but difficult to apply in initial studies of field upgrading processes based on thermal cracking where sample size is too small to separate the vacuum residue and measure its properties.

The viscosity of heavy oils is highly dependent on the content of vacuum residue [6] and its properties, which are difficult to characterize by conventional methods for petroleum distillation fractions because the boiling points can only be extrapolated. Thermal cracking breaks portions of the largest molecules to generate solvent from the crude oil itself, thereby lowering the viscosity of the product blend [7]. Viscosity of heavy oil is also sensitive to the asphaltene fraction within the vacuum residue fraction [8]. The mass of asphaltenes tends to rise during thermal cracking before the onset of coking [9], and the interactions between these colloids change giving a progressive reduction in stability of the products [7]. As a result, the asphaltene fraction can correlate with the performance of thermal cracking processes such as visbreaking [10]. Consequently, the heaviest fractions in heavy oil can be chemically altered by the thermal cracking, but the ability to capture

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Nomenclature

a	parameter in Mehrotra [19] viscosity correlation
a, b, c	stoichiometric coefficients in kinetic model introduced by Ayasse et al. [11]
A, B	adjustable parameters in Riazi [12] method
k'	rate constant in kinetic model, h^{-1}
n	number of experimental measurements or number of reactions
SG	specific gravity
SG_0	adjustable specific gravity parameter in Riazi [12] method
SG^*	normalized specific gravity in Riazi [12] method
t	reaction time, h
T	temperature, K
T_b	mean boiling point or 50% boiling point, K
T_0	adjustable temperature parameter in Riazi [12] method
T^*	normalized temperature in Riazi [12] method
x	mass fraction
x_c	cumulative mass fraction
X	conversion

Greek Letters

α, β	parameters in Eq. (9)
μ	viscosity, cP or mPa·s
ρ	density, kg/m^3
τ	residence time, h or min

Subscripts

0	initial value, initial concentration
av	average
i	component i in a mixture
exp	experimental
F	feed, original heavy oil
fi	fraction or pseudo-component i
j	component j in a mixture
pred	prediction
VR	vacuum residue

Abbreviations

AAD	average absolute deviation
HO	heavy oil
SimDis	simulated distillation analysis
SSR	sum of squared residuals
VR	vacuum residue

such shifts in behavior is limited by the inability of normal petroleum characterization, based on correlations with boiling point and density and blending rules, to deal with such chemical alterations of the heaviest fraction.

The purpose of this study was to develop a coupled kinetic-fluid property model suitable for initial studies of potential conversion technologies. The model was then used to explore the importance of chemical alteration of the vacuum residue fraction in modeling the viscosity of the product blends. Two heavy oils were thermally cracked in batch micro-reactors. The feeds and cracked products were characterized by simulated distillation. A simple lumped-kinetic model, following well-established approaches [3], was coupled with a model for the viscosity of the heavy oil components and their blends. The hypothesis was that the chemical alterations of the heavy fractions by the thermal cracking reactions would prevent the calculation of the product viscosity as a simple re-blending of the feed fractions in their new proportions with distillable fractions formed by cracking.

2. Experimental materials and methods

2.1. Heavy oil properties

Two heavy oils were selected for this study, designated HO#6 and HO#12, with properties listed in Table 1.

Table 1
Feed properties.

Property	HO#6	HO#12
Source	Mexico	Venezuela
Gravity, API°	13.2	8.1
Total acid number	0.1	3.89
Density at 25 °C (g/mL)	0.972	1.008
Viscosity at 25 °C (cP)	14,800	289,000
Water Content, % wt after cleaning	0.12	0.21
Saturate content (wt%)	29	22.6
Aromatic content (wt%)	19.3	33.6
Resin content (wt%)	35.2	32.9
Asphaltene content (wt%)	16.7	10.8

2.2. Thermal cracking reactions

The heavy oils were subjected to thermal cracking reactions that provided experimental data for kinetic modeling, and the characterizations of the feed and products from the reactions were used as input data for the development of the fluid model. These thermal cracking experiments were carried out in 15-mL stainless steel batch microreactors fabricated from tubing fittings. The isothermal reaction conditions were provided by plunging the microreactor into a fluidized sand bath preheated to the reaction temperature. The reaction contents reached a stable temperature within 5 min, approximately 16 °C below the set point of the sand bath. All reaction temperatures are reported at the interior of the reactor. After the desired reaction, the microreactor was removed from the sand bath and quenched in cold water.

Before the reaction, the microreactor was pressurized with nitrogen to 1.38 MPa, then purged and pressurized at 0.69 MPa, respectively. After the reaction, the reactor was cooled and coke and liquid products were recovered and quantified for material balances. Coke was filtered out using 3.0 μm membrane filter papers (Millipore) and methylene chloride as solvent. The filter paper was dried in an oven at 80 °C for 24 h, and then weighed to quantify the amount of coke. Liquid products were quantitatively recovered after the filtration by removal of methylene chloride in a rotary evaporator. Simulated distillation (SimDist) analyses of both the heavy oil and the liquid products gave a quantitative estimation of the conversion of >524 °C fraction.

Reactions were made in duplicate, one of them was intended for mass balance, where the products were quantitatively collected, but the light ends were lost during the removal of methylene chloride by rotary evaporation, and the other reaction was made to collect the products without any further treatment, in order to minimize the loss of light ends. The samples from the second reaction were filtered with syringe filters to remove the coke, and were used for viscosity measurements and SimDist analysis.

2.3. Characterization of feed and products

Heavy oil feed and liquid products were analyzed by Simulated Distillation (SimDist). A modified ASTM D6352 method was set up