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Dependence of onset time for mesophase formation on operating parameters during catalytic hydroconversion of Athabasca vacuum residue

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ABSTRACT

During the catalytic hydroconversion of vacuum residue fractions of bitumen or petroleum, the formation of mesophase can lead to fouling of reactor internals. In this study we examine the dependence of the onset of mesophase in a batch microreactor designed to enable in situ microscopic observation of the reacting liquid. The following process variables were investigated: temperature, partial pressure of hydrogen, catalyst concentration, agitation speed, and their interactions. Athabasca vacuum residue was converted in the presence of an iron sulfide particulate catalyst, and a statistical model was developed to describe the effects of the process variables on the onset time for mesophase formation. The temperature and catalyst concentration, respectively, had the most effect on mesophase onset time. The time for mesophase formation dropped by 12.1 min when the operating temperature increased from 440 °C to 450 °C. The mesophase onset time increased by 7.4 min when 3 wt.% of catalyst was added at 440 °C, compared to no catalyst addition. Partial pressure of hydrogen was not significant as an independent process variable for the range studied, from 2.4 to 5.2 MPa. The combined effects of hydrogen partial pressure and catalyst concentration were significant, as were the combined effects of temperature and catalyst concentration.

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1. Introduction

The depletion of conventional petroleum coupled with increased demand is making upgrading of bitumen and heavy oil more attractive for refineries [1]. Hydroconversion uses elevated temperatures of 400–450 °C and hydrogen pressures of 7–25 MPa to simultaneously thermally crack and catalytically hydrogenate the vacuum residue components to produce good yields of lighter oil fractions [2,3]. The main function of the hydrogen and catalyst is to prevent the formation of insoluble coke by hydrogenating the cracked products of the thermal reactions, thereby suppressing addition reactions [4]. Within hydroconversion reactors, coke plays a leading role in catalyst deactivation and fouling of reactor internals, while sediment formation downstream of the reactors often limits the conversion [5].

In petroleum processing, coke is normally defined as an insoluble thermal product. The formation of coke involves a complex combination of cracking, addition, condensation and aromatization reactions which results in the formation of a new carbonaceous phase [4], so that phase behavior is an important aspect of coke formation [6,7]. Carbonaceous mesophase is a subset of the coke phases that form during processing of vacuum residue, which is distinguished by its optical anisotropy [8]. Mesophase is a liquid crystalline phase which is consisted of planar aromatic molecules with significant orientational order but no long range positional order [9]. Although components in the heavy oil can form liquid crystals at much lower temperatures [10], mesophase formation in heavy oil requires modification of the initial components by thermal reaction. Mesophase exhibits optical anisotropy and is generally first observed after spherules nucleate in the liquid phase. The size of the spherules depends on the operating conditions of the reactor, such as the temperature, pressure, mixing, and the chemical properties of the feedstock. Subsequently, the spherules can grow in size to hundreds of micrometers by coalescence with time to form bulk mesophase, if their viscosity and the viscosity of the medium remain low [11].

The texture of mesophase is defined as the pattern of light and dark regions when viewed under cross-polarized light, which causes the mesophase to exhibit colored regions corresponding to different alignments of the component molecules [12]. Optical texture depends on the chemical makeup of the feedstock. For example, compounds in the feed that are rich in hydrogen yield coke with large anisotropic domains. In contrast, compounds rich in polar groups such as oxygen, sulfur, and other heteroatoms form coke with fine grained mosaic texture [13]. The mesophases from vacuum residues of bitumen or petroleum, and from coal pitches are classed as a discotic nematic liquid crystals [9,14]. Further heating results in the formation of large domains of coke with size >25 μm, and a very minor component forms with either a mosaic

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or fibrous texture when observed under cross-polarized light [13]. The presence of hydrogen at high pressure enhances the fluidity of the coke material, giving much larger domains of mesophase [15]. Honda [16] found that temperature, residence time or reaction time, heating rate, gas flow rate, and stirring all influence the formation of mesophase.

The formation and growth of mesophase can be studied in situ at high temperature and pressure through a transparent window using optical microscopy with cross-polarized light [17]. Several studies have used in situ microscopy to study cracking of heavy oils and bitumen under flowing nitrogen at pressures ranging from 1.7 to 13.8 MPa [18]. Under these conditions, the size of the mesosphere domains remained small (a few micrometers in diameter), and the resulting coke was viscous and virtually impossible to deform, even at 440 °C [18]. In situ observation of mesophase formation with hydrogen atmosphere is essential in order to mimic the process conditions in heavy feeds hydroconversion reactors.

In this paper we examine the onset of mesophase formation during catalytic hydroconversion of Athabasca vacuum residue using a hot-stage inverted micro-reactor. The micro-reactor apparatus allows the examination of the effects of temperature, partial pressure of hydrogen, catalyst concentration, agitation speed, and the effect of their interactions on the onset time for mesophase formation. Although the cracking reactions typically follow first-order kinetics [3,4], the onset of observable mesophase results from a combination of reactions, phase behavior, agglomeration, and coalescence of anisotropic domains [6,8]. Consequently, a statistical model is developed to allow for quantification and assessment of significance of the effects of the process variables.

2. Theory and mathematical modeling

In this study a linear model is developed for the onset time for mesophase formation. Given a data set of n independent measurements, a linear regression model assumes that the relationship between the dependent variable y_i (mesophase onset time in this study) and the p-vector of process variables x_i is approximately linear. The model takes the form:

$$Y = X\beta + \varepsilon \tag{1}$$

where

$$X = \begin{bmatrix} 1 & x_1(1) & \cdots & x_i(1) & x_1(1)x_2(1) & x_1(1)x_i(1) & x_2(1)x_3(1) & \cdots & x_i(1)x_j(1) & \cdots & x_1(1)x_2(1)x_i(1) & \cdots & x_i(1)x_j(1)x_k(1) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & x_1(n) & \cdots & x_i(n) & x_1(n)x_2(n) & x_1(n)x_i(n) & x_2(n)x_3(n) & \cdots & x_i(n)x_j(n) & \cdots & x_1(n)x_2(n)x_i(n) & \cdots & x_i(n)x_j(n)x_k(n) \end{bmatrix}$$

$$\beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_{12} \\ \beta_{1i} \\ \beta_{23} \\ \vdots \\ \beta_{ij} \\ \vdots \\ \beta_{12i} \\ \vdots \\ \beta_{ijk} \end{bmatrix}, \quad Y = \begin{bmatrix} y_1 \\ \vdots \\ y_n \end{bmatrix}, \quad \varepsilon = \begin{bmatrix} \varepsilon_1 \\ \vdots \\ \varepsilon_n \end{bmatrix}.$$

The index n indicates the observation number, where $i \neq j \neq k$ and no repeated terms are allowed, e.g. either x_1x_2 or x_2x_2 is allowed in the matrix, but not both. Each element of the matrix X is not considered as random variable, which is simply observed, but rather it has predetermined fixed values, which are chosen in the experimental design. β is a vector of the regression coefficients. The statistical value of the model and conclusions about the effects of variables are inferred from the β values. The error or disturbance term ε captures all other factors that influence the dependent mesophase onset time Y, other than the process variables in X.

In this study, the function *regress* in the MATLAB software package was used to estimate the parameters, β, subject to ordinary least-squares minimization. The closed-form expression for the estimated value of the unknown parameter β is:

$$\hat{\beta} = (X'X)^{-1}X'Y \tag{2}$$

where $\hat{\beta}$ is a vector of the estimated variable coefficients, i.e. the unit process effects, found from ordinary least-squares minimization. In contrast, β is the actual exact unknown vector of the true values of the variable coefficients when there are no errors. For such a linear model, the coefficient of multiple determinations is given by:

$$R^2 = c'R_{xx}{}^{-1}c \tag{3}$$

where c is a vector of the cross correlations between the process variables and the dependent mesophase onset time, c' is the transpose of the vector c, and R_{xx} is a matrix of the inter correlations between the process variables.

The process variables will take a value between -1 and $+1$, i.e. the value of each process variable is relative to other values of the same process variable. The value -1 represents the lowest value of a process variable and $+1$ indicates the highest value of that process variable. The value of a relative process variable is given by the generic formula:

$$\tilde{Z} = \frac{Z - \overline{Z}}{(Z_{high} - Z_{low})/2} \tag{4}$$

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