



Predictive correlations for thermal upgrading of petroleum residues



Mohammad Ghashghaei*

Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, P.O. Box 14975-112, Tehran, Iran

ARTICLE INFO

Article history:

Received 4 October 2014

Received in revised form 8 August 2015

Accepted 12 August 2015

Available online 18 August 2015

Keywords:

Vacuum residue
Atmospheric residue
Thermal upgrading
Cracking
Pyrolysis
Kinetic modeling
Correlations
Visbreaking
Delayed coking
Heavy fractions

ABSTRACT

Predictive correlations are presented for thermal conversion of petroleum residues employing a large number of data points obtained from the literature. The proposed correlations include equations adopted in terms of three operating variables of temperature, reaction time, and pressure and three main characteristics of a residuum including API, sulfur content, and CCR to predict upgrading conversion, liquid yield, gas yield, sulfur content of the liquid product, and yield of heavy gas oil. The expressions employed in these correlations were carefully chosen from a large group of functions with a minimum number of regression variables. The trends of the dependent variables in terms of the six independent modeling variables are discussed. Satisfactory statistical results were achieved for all correlation models presented, indicating their applicability to different types of residues over a wide range of operating conditions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The bottom-of-the-barrel conversion technologies in petro-refining industry have made progress under the pressure of a pair of conflicting facts: (1) the crude oil resources becoming heavier and more contaminated with sulfur and metals, and (2) the increasing demand for higher quality fuels [1]. Various upgrading strategies exist to convert heavy oils to valuable products. The so-called carbon rejection or thermal processing routes are the most widely used in refineries owing to their simple operation, lower cost, and flexibility to handle any type of residue [2–5]. Thermal upgrading technologies have accounted for about 64% of the worldwide residue processing capacity [2]. Excellent reviews have been published on visbreaking [3–5] and delayed coking [6–8] which address the chemistry, kinetics, and/or economics of the process.

Reliable reaction models developed from rigorous pilot plant experiments are central to simulation and design of heavy petroleum upgrading units. There are three modeling approaches for this purpose including kinetic modeling, stochastic Monte Carlo method, and empirical modeling, as briefly reviewed in [8].

Lumping is widely used for the kinetic modeling of upgrading reactions of heavy oils as it is arduous to describe the kinetics at a molecular level [9]. A first-order power-law expression is usually found to describe the kinetics of upgrading satisfactorily with a reaction rate constant obeying a standard Arrhenius-type temperature-dependence [9–15]. At high conversions, however, the polymerization reactions may upset the first-order kinetics [9].

Considerable research has been devoted to the kinetic modeling of visbreaking with the lumping approach as reviewed in [3,4] where the product yields are presented in terms of the quadruple classification of heavy oil components including saturates, aromatics, resins and asphaltenes (SARA). As concluded by Singh et al. [4] a five-lump kinetic model established on the basis of the delplot approach [16] can successfully predict the experimental data.

Through an improvement made to the structure-oriented lumping approach, a reaction kinetic model has been expounded [17,18] to identify the molecular composition of the residuum and further to predict the product distribution of delayed coking. Elaborate information on the residue was apparently required that included density, molecular weight, elemental composition, group composition, boiling range, metal content, and carbon residue [17,18]. The proposed model was found to be reliable in the temperature range of 460–500 °C [17] which is the usual conditions in this process.

Taking into account the sophistications engaged in fundamental modeling of complex reactions occurring in thermal upgrading

* Fax: +98 21 44787032.

E-mail address: m.ghashghaei@ippi.ac.ir

Nomenclature

a, b, \dots, k	correlation constants
API	API gravity, °
As	asphaltenes or <i>n</i> -heptane insolubles, wt%
CCR	conradson carbon residue, wt%
d	density
FI	feed index
G	gas yield, wt%
GO	total gas oil yield, wt%
HGO	yield of heavy gas oil, wt%
HS	hydrogen sulfide, wt%
L	liquid yield, wt%
LGO	yield of light gas oil, wt%
Min AD	minimum absolute deviation
Max AD	maximum absolute deviation
MAD	mean absolute deviation
MAPE	mean absolute percentage error
N	naphtha yield, wt%
NA	naphthenic aromatics, wt%
<i>n</i> -C ₅	<i>n</i> -pentane insolubles, wt%
P	pressure, bar
PA	polar aromatics, wt%
R	resid yield, wt%
R^2	coefficient of multiple determination
R^2_{adj}	adjusted coefficient of multiple determination
R^2_{CV}	predicted squared correlation coefficient
Rs	resins, wt%
S	sulfur content, wt%
Sa	saturates, wt%
SG	specific gravity
SI	severity index
Sum	summation of the estimated yields
t	reaction time, min
T	temperature, °C
X	conversion, %
x	visbreaking conversion, %
y	response dependent variable

Greek letters

φ	feed index
ψ	severity function

Subscripts

<i>est</i>	estimated
F	feed
G	gaseous product
GO	gas oil
L	liquid product

of residual oils, and complexities with accurate characterization of the large molecules involved as well as the reaction pathways through which they are converted, empiric models and correlations are widely used as a reasonable choice. A number of correlations have been suggested in the literature by different groups of authors in terms of API or CCR for conversion modeling or in terms of sulfur percent for obtaining the sulfur content of the products [9]. The interplays of these influencing factors are not represented adequately by the existing models. In other words, the correlations available often present an equation in terms of one or two factors at other variables taken as constant. This limited use of correlative factors and the empirical nature of the correlations make it risky to apply the models beyond the range of feed properties or operating conditions at which they were derived.

Table 1

Correlations available for visbreaking of residual oils.

Fahim et al. correlations ^a		
Product (wt%)	Yield expressions	Sulfur expressions
G	$0.189825x + 0.677163$	$(32/34) HS$
N	$0.738321x + 0.260174$	$0.260112 S_f$
R	$-0.146668x^2 - 2.203644x + 98.677947$	$S_f - S_n - SS_G$
HS	$0.02023x + 0.06043 S_f - 0.156$	—
GO	—	$0.539924 S_f$
Kataria et al. correlations ^b		
Product (wt%)	Yield expressions	
G	$0.43 SI (n-C_5/CCR)^{0.45}$	
N	$0.271 SI (As/PA)^{0.19}$	
LGO	$3.24 SI^{0.77} (Sa/NA)^{0.13}$	
HGO	$4.76 SI^{0.5} [n-C_5/(S + CCR)]^{0.96}$	
R	$100(As/Sa)^{0.02} \exp[-0.023(1 + n-C_5/CCR)SI]$	

^a Herein G is gas yield (wt%), N is naphtha yield (wt%), R is resid yield (wt%), HS is yield of hydrogen sulfide (wt%), GO is gas oil yield (wt%), and x is conversion which is defined as the summation of $G + N$ (wt%).

^b The severity index SI has been defined as $SI = t \exp[-(E/R)/(1/T - 1/700)]$ with t the reaction time (s) and T the reaction temperature (K); *n*-C₅ is *n*-pentane insolubles (wt%), As denotes asphaltenes or *n*-heptane insolubles (wt%), PA shows polar aromatics (wt%), Rs shows resins (wt%), Sa shows saturates (wt%), HGO is heavy gas oil with boiling range of 350–500 °C (wt%), LGO is light gas oil with boiling range of 150–350 °C (wt%), NA is naphthenic aromatics (wt%), and S is the sulfur content of the residue feedstock (wt%).

Relatively scant attention has been paid in earlier works on visbreaking to extend empiric models that might be used over a wide range of input variables. There have always been general guidelines for controlling the severity of the reactions, however. For example, a relevant study [19] states that for vacuum bottoms with concentrations of insoluble matter in *n*-C₇ below 18%, the controlling variable with respect to severity of operation is residence time, while for feeds with asphaltene concentrations above the aforementioned level, the variable that allows better control is the reaction temperature.

Recently, the reactivity of several vacuum residues was evaluated by Stratiev et al. [20] who observed that the compositional data from SARA tests are considered insufficient information for assessment of a residue thermal reactivity and colloidal stability.

One of the correlation models available for visbreaking is the expressions by Fahim et al. [15] which are summarized in Table 1. These correlations require conversion level as an input variable while conversion is itself defined to be the summation of the yields of gas and naphtha. This empiric model gives no expression for evaluation of conversion in terms of feed properties or operating conditions. Furthermore, the equations listed here have been obtained from data with conversion levels ranging from 3.8% to 15.69% which are relatively low compared to those in commercial practice [9].

Another empiric model of visbreaking has been presented by Kataria et al. [3,12] who considered the following overall functionality for the product yields:

$$y = f(SI, FI) \quad (1)$$

where SI and FI represent separate indices for severity and feed properties, respectively (see Table 1 for more details). These correlations are helpful in prediction of product yields provided that the feed SARA fractions are known. However, this characterizing test is lengthy and expensive. Alternative correlations that employ readily available properties of the residuum are then worth exploring.

In most of the existing correlations, such as those presented in Table 1, the sulfur content of the liquid product is only modeled with the sulfur concentration on the feed, as also stressed by Ancheyta [9]. It is believed, however, that total sulfur in the feed is not all data required to describe even the effect of feed type on the sulfur distribution and some other complicating factors exist that hinder a general correlation for any kind of residue [7]. It

Download English Version:

<https://daneshyari.com/en/article/1197107>

Download Persian Version:

<https://daneshyari.com/article/1197107>

[Daneshyari.com](https://daneshyari.com)