Fuel 106 (2013) 498–504

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Studies on the preliminary cracking of heavy oils: Contributions of various factors

Wenzhe Chen, Dongmin Han, Xiaohui Sun, Chunyi Li *

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266555, China

HIGHLIGHTS

- ▶ A methodology was established to study the preliminary cracking of heavy oil.
- ▶ A new reaction route was proposed concerning the participation of zeolite pores.
- ▶ An active matrix is effective in the cracking of aromatic components.
- ▶ The apparent effect of thermal reactions may be negative for heavy feeds.

ARTICLE INFO

Article history:
Received 23 April 2012
Received in revised form 28 December 2012
Accepted 31 December 2012
Available online 23 January 2013

Keywords:
Preliminary cracking
Contribution
Zeolite
Thermal reactions
Active matrix

ABSTRACT

The preliminary cracking (pre-cracking) of heavy oils has been studied on a typical fluid catalytic cracking catalyst. Contributions of several factors were evaluated, including those of zeolite, thermal reactions, and active matrix. Results indicate that zeolite (REUSY) plays a leading role in pre-cracking and its contribution always accounts for more than 50%. In highlighting the remarkable effect of zeolite, a new hypothetical reaction route, namely the relay of active sites, is proposed for the consideration of zeolite internal surface. The contributions of thermal reactions and active matrix change with the contents of aromatic components in different feeds. The active matrix is effective in pre-cracking of large hydrocarbon compounds with aromatic rings; its contribution increases with the aromaticity of the feed. For naphthene- or medium-based feeds, the active matrix can boost pre-cracking significantly, and too many thermal reactions are disadvantageous in this case. For paraffin-based VGO, excessive matrix activity will result in the over-cracking of desired products.

1. Introduction

Crude oils around the world are becoming heavier, and thus, treating light feeds with fluid catalytic cracking (FCC) technology is unprofitable [1]. Many studies in this field are oriented toward the efficient conversion of heavier feeds, such as heavy gas oil (HGO) and vacuum residue (VR). In this regard, a definition of “preliminary cracking” is proposed.

The restricted aperture of USY zeolite confines its catalytic property in the catalytic cracking of heavy oil [2]. Although the free pore diameter of USY zeolite is only 0.74 nm, molecules with a critical molecular size larger than 0.74 nm can still be diffused into the pore structure due to the nature of three-dimensional supercage in zeolite USY and the deformable ability of diffusate molecules. However, effective diffusion coefficients decrease by four orders of magnitude for molecules with critical sizes from 0.675 nm to 0.92 nm [3]. De Lasa mentioned that zeolite Y has a critical size cutoff point of 1.02 nm, and hydrocarbon molecules with critical sizes larger than the critical size cannot penetrate into intracrystalline pores [4]. Thus, large molecules with critical diameter of more than 1 nm cannot easily access the micropores of zeolite Y or USY. Chen [1] reported that critical diameters of paraffins and aromatics in VGO with boiling point higher than 644 K (371 °C) are all larger than 1.2 nm; a simulation method indicated that most molecules in heavy feedstocks are too large for zeolite pores. Otterstedt [5] and Thomas and Bramby [6] pointed out that in FCC, large molecules in heavy oil need to be cracked outside the zeolite pores into moderate ones that could be diffused into the zeolite pore system. They referred to this process as “preliminary cracking” or “pre-cracking.” In this context, Akzo Nobel used the “accessibility” of active centers in the design of new catalysts in heavy oil cracking; this method achieved fairly viable results [1].

Many research findings support the key role of zeolite in the pre-cracking of VGO, including those by Thomas and Barmby [6] and Corma [7,8]. Moreover, an active matrix containing alumina is widely acknowledged [9,10] to be effective in promoting heavy oil conversion. Accordingly, both zeolite and matrix contribute to the pre-cracking process. Thermal reactions also inevitably occur at the set temperature for operation, which contributes to the pre-cracking process as well.

---

* Corresponding author. Tel.: +86 0532 86981862.
E-mail addresses: chili_upc@126.com, chyli@upc.edu.cn (C. Li).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.12.090

In general, the significance of pre-cracking has been acknowledged. However, few systematical studies have been conducted on this subject, and thus will be the focus of the present paper. Several issues are considered in this work, including the appropriate range of pre-cracking, the contributions of zeolite, the active matrix, and the thermal reactions in pre-cracking, as well as the interactions among these factors for various feedstocks. We attempted to establish a method for assessing the contributions of several factors to pre-cracking, and to determine an appropriate law based on these results to facilitate the design of FCC catalysts for heavy oils with different properties.

The cracking of heavy hydrocarbons on industrial catalysts is a comprehensive process in which reactions on the zeolite and matrix proceed simultaneously, meanwhile thermal and catalytic cracking cannot be separated. In investigating the three factors separately, a specific condition was created to make the feeds react on the matrix and zeolite in sequence. Inert sand with the same volume of matrix or zeolite was used to investigate the influence of thermal reactions. Thus, the contributions of zeolite, matrix, and thermal cracking could be evaluated with the help of conversion data. Thermal cracking is referred to as the reactions on inert sand used as substitutes for those on the zeolite and matrix. The contribution of zeolite was evaluated with the experimental data when only zeolite is present. The contribution of active matrix is referred to as the excess part after the matrix was loaded on top of the zeolite layer. Thermal reactions on the zeolite and matrix were deducted in the evaluation of contributions of zeolite and matrix. Although this method cannot accurately reflect the industrial cracking process and even the experimental situation, it provides a quantitative means to investigate the influence of zeolite, matrix, and thermal reactions separately, whereby the composition of a FCC catalyst could be chosen accordingly on the basis of the feed property.

2. Materials and methods

Two experiments were designed to search for an appropriate range of pre-cracking and to investigate the contributions of several factors to pre-cracking. All reactions were carried out on fixed-bed reactors, in which catalysts could be loaded in different layers. The entire process was maximum gasoline-oriented from heavy feedstocks. In the first experiment, a representative medium-based VGO (feed B, Table 1) was selected to ensure that a representative range for pre-cracking could be obtained. Next, 1.000 ± 0.005 g feed oil was passed through a series of reactors at the same temperature (500 °C) with different loadings of catalysts, from 0.4 g to 2.0 g of pure zeolite particles. The results will be discussed later.

A group of fixed-bed reactors (Fig. 1) were used in the second experiment to evaluate the contributions of zeolite, active matrix, as well as thermal and catalytic reactions. Active matrix and zeolite particles were prepared separately with the same composition in a typical FCC catalyst, and were then loaded in a certain order as shown in Fig. 1. Thermal reactions were substituted by reactions in the same condition on an equal volume of quartz sand with the acidic catalyst. Only zeolite was loaded in the first reactor, whereas a layer of quartz sand or active matrix was loaded above zeolite in the second and third reactors, respectively. In the present study, quartz sand was considered as an inert matrix. In the last reactor, thermal reactions were determined independently without considering the effect of the matrix.

2.1. Selection and evaluation of parameters

Parameters were chosen based on their capability to reflect the level of pre-cracking accurately. Considering the pre-cracking is the first and essential step in the entire reaction. Thus, a definition of conversion was selected to bear this task. The fractions were set in a boiling range below 623 K (350 °C) as calculable products because the largest critical diameter of the product molecules was around 1 nm, which approached the cut-point diameter of zeolite USY [4].

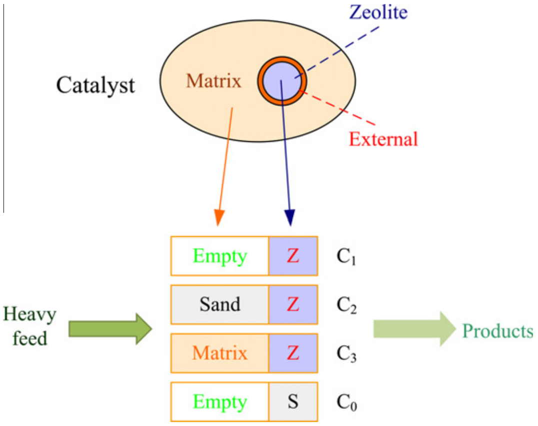

Fig. 1. Different ways of packing in the experiment (C_0–C_3 represent various conversions; Z-zeolite; S-sand).

Table 1
Properties of feedstocks.

Feeds	Density (ρ) (g/cm^3)	Fraction below 623 K (wt%)	SARA composition (wt%)		
			Saturates	Aromatics	Resins + asphaltenes
A	0.86	0.04	85.9	11.5	2.6
B	0.93	5.6	65.5	20.7	13.8
C	0.96	13.1	51.0	45.5	3.5

Several parameters were defined in the second experiment. C_0–C_3 represented conversions of heavy oil in four reactors (Fig. 1). R_Z and R_M referred to the contributions of zeolite and active matrix to pre-cracking, and R_T, R_C were related to the contributions of total thermal and catalytic reactions, respectively. Evaluation formula and the correlations of these parameters are as follows:

$$R_T = (C_2 - C_1 + C_0)/C_3, \tag{1}$$

$$R_Z = (C_1 - C_0)/C_3, \tag{2}$$

$$R_M = (C_3 - C_2)/C_3, \tag{3}$$

$$R_C = R_Z + R_M, \tag{4}$$

$$R_Z + R_M + R_T = R_C + R_T = 100\%, \tag{5}$$

where C_3 is the conversion when zeolite and active matrix are both present, and C_1 is the conversion when only zeolite is present. Thermal reactions consisted of two parts, C_0 and (C_2–C_1). C_0 is easy to understand, and (C_2–C_1) refers to the excess part of the conversion relative to C_1 for the presence of the matrix. Thus, R_T could be obtained through Eq. (1). The effect of thermal reactions was not considered in the evaluation of R_Z and R_M, thus $R_C = R_Z + R_M$, $R_Z = (C_1–C_0)/C_3$, and $R_M = (C_3–C_2)/C_3$ (Eqs. (2)–(4)). R_M only equaled the extra contribution $(C_3–C_2)/C_3$ when the active matrix was loaded on top of the zeolite layer compared with that when none was loaded above (Eq. (3)).