Chemical Engineering Journal 329 (2017) 275–282

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Cracking of heavy oil residues in a continuous flow reactor, initiated by atmospheric oxygen

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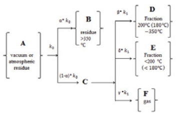
HIGHLIGHTS

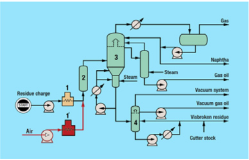
- Thermo-oxidative cracking of heavy oil residues doubles the yield of light fractions.
- Model of the process based on nonvolatile intermediate formation describes all the experiments.
- Only a small air supply to the cracking camera is needed for industrialization of the process.

GRAPHICAL ABSTRACT

The scheme of thermo-oxidative cracking:



Transformation of The Shell Visbreacking Process to thermo-oxidative cracking:



ARTICLE INFO

Article history:
Available online 17 May 2017

Keywords:
Heavy oil residues
Thermo-oxidative cracking
Visbreaking
Yields of light hydrocarbon fractions
Thermal destruction of hydrocarbons
Modelling

ABSTRACT

The article presents the results of processing heavy oil residues initiated by atmospheric oxygen. We found that the introduction of a small amount of atmospheric oxygen (2–6%) in the thermo cracking reactor (thermo-oxidative cracking) significantly increases the yields of light fractions. E.g. A thermo cracking of vacuum residue (visbreacking) with the air supply to the soaker camera gives twice more light fractions than traditional visbreacking process (36% of petrol and diesel fractions compared to 10–15% in conventional process). Thermo-oxidative cracking of atmospheric residue gives up to 60% of light fractions. In order to obtain a mathematical description of the process needed for its subsequent industrial implementation we conducted experiments on thermo-oxidative cracking of atmospheric and vacuum residues in a continuous flow reactor with a wide variation of the process parameters. Based on the analysis of the experimental data a common scheme for thermo-oxidative cracking, a mathematical model of the process and its parameters were established. The model adequately describes all the experimental data obtained in the temperature range 430–460 °C, pressure 2–8 atm, retention times 4–33 min and relations oxygen/raw material 0,9–2,5 % wt. Industrial implementation of thermo-oxidative cracking needed just minimal modification of the existing thermal installations through the organization of air supply in the soaker chamber. This modification will increase the output of light fractions in the thermal processing heavy oil residues in 2–3 times with minimal capital investments.

1. Introduction

Currently in the world there are different technologies for the processing of heavy oil residues, which allows increasing the depth of oil refining. Since the 80-ies of the last century the visbreacking process of vacuum residue used. The visbreacking process is carried out at the temperatures 430–460 °C under pressure to 3 atm in a tube furnace or in a soaker chamber [1,2]. In the latter case, a tubular furnace is used only for heating of the feedstock. Products of visbreacking are gas, light fractions (gasoline and diesel) and heavy residue with a reduced viscosity suitable for use as a boiler

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http://dx.doi.org/10.1016/j.cej.2017.05.104
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fuel. The yield of light fractions does not exceed 10–15% [2,3]. Significantly increase the yield of light fractions (mainly diesel) allow the processes of hydrocracking, which is carried out at a temperature of 400 °C and a pressure of 50–100 atm using, as a rule, several reactors. Formed in this process, the heavy hydrocarbon fraction is used as raw material for catalytic cracking [4]. The disadvantage of this way of deepening oil processing are prohibitively high capital and operating costs.

We managed to find a way of an intensification of processes thermo destruction processing of heavy oil residues (vacuum and atmospheric residues), which, besides accelerating the process, conducts to increase of depth of oil refining with additional quantities of hydrocarbon gases, gasoline and diesel fractions. Heavy residues produced in the thermo-oxidative cracking process suitable for use as boiler fuel or bitumen [5,6]. The essence of the developed method is to initiate the process by atmospheric oxygen when mixed with heavy oil residues before soaker camera at the temperature of the feed stream 430–460 °C and a pressure not higher than 10 atm.

The inclusion of the developed thermo-oxidative processes in scheme of oil processing will allow extracting from the heavy oil residue from 30 to 60% light fractions and fuel oil or bitumen of the required quality [7]. Received at the installation with a continuous flow reactor the results of thermo-oxidative cracking of heavy oil residues of different composition and origin have shown the feasibility of using this method for deeper processing of oil with low capital investments and production costs [8,9]. According to the results of our previous studies [5–9], the products and optimal parameters of the processes of thermal-oxidative cracking of various vacuum residues are close to each other. The results of thermo-oxidative cracking of atmospheric residues of different kind under comparable conditions are also similar. However, the difference in the results of cracking of vacuum and atmospheric residues is more significant. For this reason, for a deeper understanding of the mechanism of reactions occurring and the subsequent modelling of industrial reactor, we choose thermo-oxidative cracking of vacuum and atmospheric residues which have the most difference in a wide range of process parameters.

2. Materials and methods

As examples of atmospheric and vacuum residues we used vacuum residue from Moscow oil refinery and atmospheric residue from Ryazan oil refinery as. Physical-chemical characteristics of the starting materials are shown in Tables 1 and 2.

The scheme of the installation of thermo-oxidative cracking of heavy oil residues with a continuous flow reactor is presented in Fig. 1. The raw feedstock from container C_1 with a volume of 40 liters, which is equipped with safety valve SV_3 for emergency depressurization and a ball valve for run-off of the feedstock with temperature 60-120 °C and a plunger-type, proportioning pump (PPP) was fed into the heater H_1. In order to prevent congelation of the feedstock, container C_1, the head part of the PPP, the connecting piping, as well as tap T_1 were heated with external electric heaters.

Table 1
Physical-chemical characteristics of vacuum residue of the Moscow oil refinery.

Density at 20 °C, kg/m^3	1002
Mechanical impurities content, %wt	0,2
Conventional viscosity, °CV	139,9
Fractional composition (initial boiling point, 419 °C)	
The share of distillate, % volume	Boiling temperature, °C
5,0	490
8,5	500
The structural-group composition, % wt	
Saturated hydrocarbons	9,48
Aromatic compounds	67,14
Resins	16,62
Asphaltenes	6,76

Table 2
Physical-chemical characteristics of atmospheric residue of the Ryazan oil refinery.

Mass fraction of sulfur, %wt	2,55
Flash temperature in open crucible, °C	118
Density at 20 °C, kg/m^3	946
Kinematic viscosity at 100 °C, mm^2/s	22,2
Fractional composition (initial boiling point, 214,6 °C)	
5%	314,7
10%	351,5
Output up to 350 °C, % volume	9,8
Output up to 360 °C, % volume	11,1

Furnace F_1 heated the raw feedstock to the operating temperature 430–460 °C. In order to increase the rate of heat transfer, furnace oil was stirred with blade mixer by means of electrical drive ED_2 with the rate of rotation of 3000 rev/min. The feedstock was then fed into reactor R with the active volume of 1,5 L, which maintained the temperature within the limits of 430–460 °C via electric trace heating. The pressure and the liquid level in the reactor were regulated with two valves V_2 и SV_1 according to the position of float gage and the pressure gage readings. The reactor was also equipped with safety valve V_1 for emergency depressurization.

At zero time, i.e. during the heating of the reactor, a distribution device was used to supply fixed doses of nitrogen to its lower part from cylinder C_1 and when the process was stabilized, the supply of nitrogen was switched off and air was delivered from cylinder C_2. Air was supplied at a rate which excludes the appearance of oxygen at the reactor outlet. In most experiments, the amount of water formed during the conversion corresponds to all oxygen fed into the reactor. So, explosive concentrations in the reactor zone were excluded. The gases supplied to the distribution device had been previously heated to the temperature of the reaction (430–4600 °C) in the electric furnace F_2, and the gas flow was controlled with variable area flow meters and regulated by valves V_4–V_7.

The cracking residue was collected from the reactor according to the level with the help of valve V_2 and sent to heat exchanger HE_1, where it was cooled to 100–150 °C and collected in receiving tank RT_1. Reaction gases mixed with nitrogen were deflected from the upper part of the reactor through V_1, which also played the role of the pressure controller in the reactor. The pressure in the reactor was adjusted so that the exhaust gas temperature does not exceed 280 °C and maintained within 0.1 atm. Then the exhaust gases were gradually channeled to refrigerating condenser C_2 and refrigerator H_1. There all the liquid products of the reaction were condensed and cooled to ambient temperature.

The cooled gas-liquid mixture was sent to gas-oil separator S. The gas phase which contained mostly nitrogen and cracked still gases (methane, ethane, ethylene, propane, propylene etc) was supplied to wet-gas meter, where their quantities were measured and then the gases were sent to burn. The liquid products from the separating vessel were collected in receiving tank RT_2. Liquid products collected in both tanks (RT_1 and RT_2) after the experiment were combined and analyzed for fractional composition by means of standard method.

3. Results and discussion

To compare the efficiency of thermal and thermo-oxidative cracking experiments were carried out at the installation (Fig. 1)