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INFLUENCE OF CATALYST/FEEDSTOCK RATIO ON THE YIELD OF LIGHT FRACTIONS AND COKE DURING THE CATALYTIC CRACKING TECHNOLOGY

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Abstract

The results of the effect of the catalyst circulation ratio on the yield of the gasoline fraction, wet gas, and coke in the catalytic cracking technology for the two industrial units using the mathematical model are present at this paper. The temperature mode to obtain the maximum yield of gasoline and gas is determined taking into account the feedstock composition, types of cracking catalyst, and coke yield in the processing of vacuum distillate from Kazakhstan and West Siberian oil.

Keywords: catalytic cracking; vacuum distillate; catalyst/feedstock ratio; mathematical model; prediction; gasoline; coke.

1. Introduction

Traditionally, catalytic cracking technology allows producing the components of commercial gasoline, arctic and winter diesel fuels, and gas with high content of propane-propylene and butane-butylene fraction from the heavy fraction of the vacuum distillate obtained by vacuum distillation of fuel oil via continuous catalyst regeneration [1- 4].

The catalytic cracking catalysts are synthetic microspheroidal zeolites with a particle size of 70-100 microns and highly specific surface area (100-400 m^2/g) [5-7]. Currently, intensive development of various types of synthetic zeolites provides a significant improvement of cracking catalysts and efficiency of industrial catalysts operation. The synthetic zeolites of X, Y, and ZSM-5 types are widely used. The first two types of zeolites have a similar nature and are different from the last zeolite by pore size and low Si/Al ratio. The zeolite of Y and ZSM-5 have been effecttively used in the catalytic cracking technology for many years. The distribution of the main cracking products is largely determined by the catalyst composition and zeolite component ratio [8-15].

Cracking catalyst is continuously circulated between the reactor and regenerator. Catalyst circulation rate is one of the main parameters that provide the desired process temperature and, accordingly, the desired yield and quality of cracking products. The catalyst surface generally contains from 0.5 to 0.8 wt% of coke at the outlet from the reactor. Coke is burned from the catalyst surface during continuous regeneration thereby providing the required temperature of the catalyst at the outlet of the regenerator.

Thus, the catalyst temperature is determined depending on the coke content on the catalyst surface after the riser-reactor and the operating mode of the regenerator. The operating mode of the regenerator is determined by the composition of the feedstock and operating mode of the reactor. The catalyst circulation rate in the riser-reactor-regenerator system is selected depending on the desired process temperature taking into account the catalyst temperature after the regenerator for the given quantity and quality of the cracking products.

The purpose of the research is assessment of the effect of catalyst/feedstock ratio on the yield of light fractions and coke during the catalytic cracking technology using the mathematical model.

2. Object of the research

The object of research is the industrial catalytic cracking units of the vacuum distillate obtained by vacuum distillation of fuel oil followed by hydrotreating. The vacuum distillate from the West Siberian oil with coking less than 0.6 wt.% is processed at the CC-1 unit. The vacuum distillate from a mixture of Kazakhstan and West-Siberian oil with coking less than 0.3% wt.% is processed at the CC-2 unit.

The catalytic cracking technology discussed in this paper differs mainly by the type of catalytic cracking catalyst. The catalyst from the CC-2 unit has a high content of zeolite components (Y and ZSM-5) – 31.5 and 12.0% wt.%, relative to the catalyst from the CC-1 unit (20 and 2 wt.%). The zeolite ratio ZSM-5 to Y is 0.381 for the catalyst from the CC-2 unit and 0.11 for the catalyst from the CC-1 unit.

The catalyst composition has a major influence on the yield and quality of products from the unit, together with the feedstock composition and the operating mode of the reactor (tab. 1).

Table 1. Material balance of the CC-1 and CC-2 catalytic cracking units

CC-1 unit			CC-2 unit		
Flow	Flowrate, t/day	%	Flow	Flowrate, t/day	%
Influent flow:			Influent flow:		
Vacuum distillate	6420.80	100.0	Vacuum distillate	3388.3	100.0
Derived product:			Derived product:		
Wet gas	1169.86	18.22	Wet gas	1197.10	35.33
Unstable gasoline	3756.16	58.5	Unstable gasoline	1441.70	42.55
Light gas oil	669.04	10.42	Light gas oil	309.35	9.13
Heavy gas oil	545.12	8.49	Heavy gas oil	243.95	3.4
Coke	260.68	4.06	Burn out coke	187.03	5.52
Unbalance	19.90	0.31	Unbalance	9.15	0.27

Thus, the yield of the wet gas rich in propane-propylene and butane-butylene fractions from the CC-2 catalytic cracking unit is much higher. This fact is directly connected with the composition of the cracking catalyst characterized by a high content of the zeolite ZSM-5 (the ratio of the zeolite ZSM-5/Y is equal to 0.11 for the CC-1 unit and 0.381 for the CC-2 unit). The catalyst composition from the CC-2 unit provides the high speed of the secondary cracking reactions with the formation of the gaseous products and reduction of the gasoline fraction yield (58.5 wt. %–CC-1 and 42.55 wt. %–CC-2).

The coke yield from the CC-2 unit is significantly higher (5.52 wt.%), it is directly related to the type of the cracking catalyst, feedstock composition, and operating mode of the reactor block.

The correction of the operating mode considering the feedstock composition and type of cracking catalyst is required to obtain a high yield of the light fractions from the industrial units. The cracking and polycondensation reactions significantly increase in case of the high process temperatures that result in a decrease in gasoline yield, increase in gas and coke yield on the catalyst surface.

3. Effect of the catalyst circulation on the yield of the light fractions from the catalytic cracking unit

Mathematical models of oil refining process allow predicting yield and quality of product from the industrial unit depending on technological mode parameters [16-18]. The calculations using a mathematical model of catalytic cracking were performed in order to evaluate the effect of the catalyst/feedstock ratio on the yield of the light fractions and coke during catalytic cracking. The mathematical model was based on the formalized scheme of hydrocarbons conversion in the catalytic cracking [19].

The differential equations of reactants concentration change from the contact time are based on the scheme of hydrocarbon conversion and supplemented by equation of heat balance with the initial conditions $\tau = 0$, $C_i = C_{i0}$, $T_0 = T_{cat}$, $l = 0$.

The catalyst circulation ratio is defined by the equation (1.1), it influences the contact time of the feedstock and catalyst.

$$\tau = \frac{V_{reactor}}{V_f + V_{cat}} \tag{1.1}$$

As the catalyst is a basic thermal medium for warming up feedstock to cracking temperature and compensating endothermic effect of the process, catalyst consumption is taken into account for calculating the temperature of the reaction start according to (1.2)

$$T_r = \frac{(G_{cat} c_{cat} T_{cat} - G_{cat} c_{cat} + G_f c_f T_f)}{(G_f c_f + G_{cat} c_{cat})} \tag{1.2}$$

here $V_{reactor}$ – reactor volume, m3; V_f – volume of the feedstock, m^3; V_{cat} – volume of the catalyst, m^3; G_{cat} – catalyst consumption, kg/h; C_{cat} – heat capacity of the catalyst, kJ/kg·K; T_{cat} – catalyst temperature, K; G_f – feedstock consumption, kg/h; c_f – heat capacity of the feedstock, kJ/kg K; T_f – feedstock temperature, K.

Thus, if the temperature is higher after the regeneration stage, than the catalyst/feedstock ratio can be lower. In case of increasing catalyst/feedstock ratio the contact time of the catalyst and feedstock in the reaction zone decreases, and the process temperature significantly increases.

The mathematical model allows calculating the yields of cracking products (unstable gasoline, light gas oil, heavy gas oil, and wet gas), group composition and octane number of gasoline fraction, and the content of propane-propylene and butane-butylene fractions in the wet gas.

The parameters of the operating mode for the two catalytic cracking units and composition of the feedstock for calculations with the model are shown in tab.2. The catalyst/feedstock ratio was selected on the basis of the technical specifications of the units at the constant temperature after regeneration. The temperature varies in the range from 768 to 815 K for the CC-1 unit, and from 773-813 K for the CC-2 unit.

Table 2. The parameters of the operating mode of the catalytic cracking reactor and composition of the feedstock

The process variables	CC-1	CC-2
Consumption of feedstock, m^3/h	376.62	191.97
Total consumption of steam in the reaction zone of the riser, kg/h	7799.88	13580.00
Total steam rate in the desorption zone, kg/h	7399.97	5190.00
Catalytic cracking temperature, K	793.98	796.42
Temperature at the inlet of the reactor, K	586.37	546.20
Pressure, kgf/cm^2	1.50	1.50
Temperature of the regenerated catalyst, K	962.40	942.85
Catalyst/feedstock ratio, ton $_{cat}$/ton$_{feed}$	4–7	5–8
The composition of the vacuum distillate		
Paraffins + naphthenes	65.5	73.71
Aromatic hydrocarbons	34.5	23.31
Resins	3.2	3.56

4. Results and discussion

The results of calculation for the two industrial catalytic cracking units of the vacuum distillate are shown in fig. 1-7. With increasing catalyst circulation ratio (from 4 to 7 ton cat/ton feed for the CC-1 unit and from 5 to 8 ton cat/tonfeed for the CC-2 unit), the process temperature significantly increases for the CC-1 unit from 769.6 to 814.0 K and for the CC-2 unit from 771 to 810 K. The conversion of feedstock also rises.

The yield of the gasoline fraction increases from 51.80% to 59.29 % wt. for the CC-1 unit and from 38.0 to 42.6% wt. for the CC-2 unit. With further increases in the catalyst circulation ratio the gasoline yield decreases to 58.77 wt%. – for the CC-1 unit and 42.26 wt%. – for the CC-2 unit (fig. 2,3).

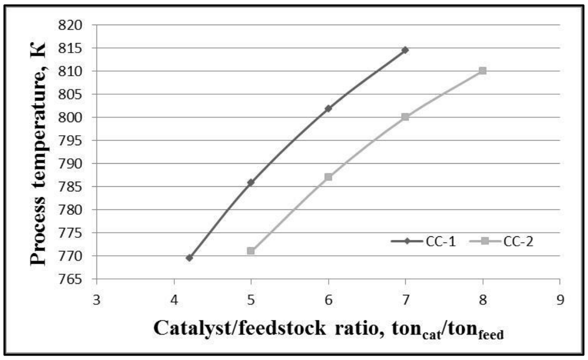

Fig. 1. Process temperature depending on the catalyst: feedstock ratio

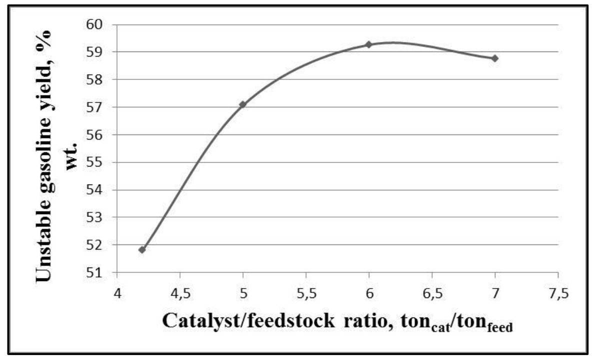

Fig. 2. The yield of the gasoline fraction depending on the ratio of catalyst: feedstock for the CC-1 unit

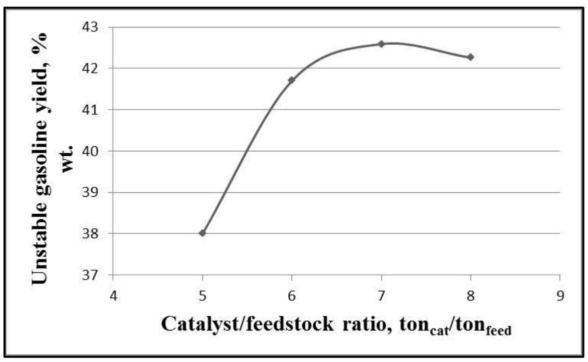

Fig. 3. The yield of the gasoline fraction depending on the ratio of catalyst: feedstock for the CC-2 unit

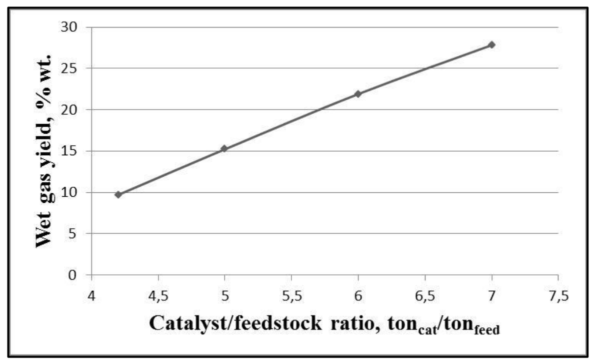

Fig. 4. The yield of the wet gas depending on the ratio of catalyst: feedstock for the CC-1 unit

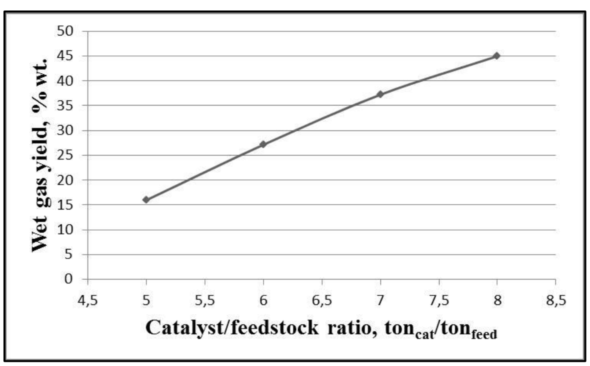

Fig. 5. The yield of the wet gas depending on the ratio of catalyst: feedstock for the CC-2 unit

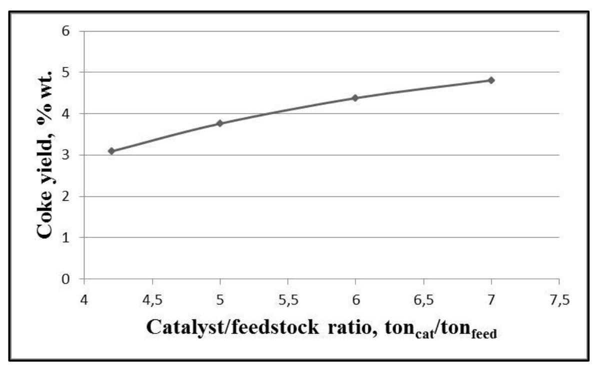

Fig. 6. The yield of the coke depending on the ratio of catalyst: feedstock for the CC-1 unit

The yield of gas and coke constantly increases (fig. 4-7) due to the secondary cracking reactions with formation of gaseous products and reactions of polycondensation and redistribution of hydrogen. For the CC-1 unit the gas yield increases from 9.70 up to 27.83 % wt., the coke yield rises from 3.09 to 4.81 %wt. For the CC-2 unit the gas yield increases from 15.95 to 44.96 wt.%, the coke yield rises from 3.74 to 6.18 wt%. The amount of coke on the catalyst surface and feedstock conversion rate are reduced with decreasing the catalyst circulation ratio.

Thus, to achieve the maximum theoretical yield of the gasoline (42.6% wt.) at the CC-2 unit is necessary to maintain the catalyst circulation ratio of 7.1 ton cat/tonfeed at the catalyst temperature after the regeneration of 962.4 K, which corresponds to the process temperature of 801K, gas and coke yields are 38.06 and 5.72% wt respectively.

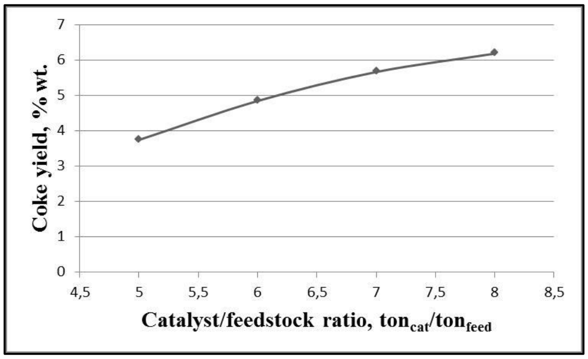

Fig.7. The yield of the coke depending on the ratio of catalyst: feedstock for the CC-1 unit

The maximum theoretical yield of the gasoline fraction at the CC-1 unit is 59.29% wt. In case of the constant catalyst circulation ratio of 6.4 ton cat/tonfeed, the catalyst temperature after regeneration of 942.85 K corresponds to the process temperature of 807.2 K.

5. Conclusions

Thus, the catalyst circulation ratio, feedstock composition, operating mode of the reactor-regenerator unit, content of the coke on the catalyst, significantly affect the temperature mode of catalytic cracking and, accordingly, the yield of the light fractions and coke.

It was determined that in case of operation on the catalyst with a high content of the zeolite ZSM-5 (the ratio of zeolite ZSM-5/Y is 0.381 for the CC-1 unit) the yield of the wet gas is significantly higher (35.33%wt.) in comparison with the CC-2 unit where it is 18.22% wt. (the ratio of the zeolite ZSM-5/Y is 0.11). The yield of the gasoline fraction from the CC-1 unit is lower (42.55% wt – the CC-2 and 58.5% wt. – the CC-1) due to the high rate of the secondary cracking reactions of hydrocarbons to form components of wet gas and condensation of aromatic hydrocarbons to coke.

The process temperature increased from 771 to 810 K with rising the catalyst circulation ratio from 5 to 8 ton cat/tonfeed during processing the high-paraffinic vacuum distillate fraction from Kazakhstan oil (CC-2). Consequently, the conversion of feedstock increased, the yield of the wet gas and coke rised to 29.0 % wt. and 2.44% wt. respectively due to an increase in the rate of secondary cracking reactions of hydrocarbons with gases formation and an increase in the rate of polycondensation reactions with coke formation. To obtain a high yield of the gasoline fraction it was necessary to ensure the process temperature of 801.2 K, it could be achieved by organizing the catalyst circulation ratio of 7.1 ton cat/tonfeed and regenerated catalyst temperature of 692.4 K, the gas and coke yields were 38.06%. and 5.72% wt.

The yield of the gasoline fraction from the CC-1 unit was maximum (59.29% wt.) in case of maintaining the catalyst circulation ratio of 6.4 ton cat/tonfeed, it corresponded to the process temperature 807.2 K, the gas and coke yields were 24.4%. and 4.57% wt. respectively.

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