ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

1 (69)

ЯНВАРЬ – МАРТ 2020 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2020

UDK 544.4:665.73/75

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DETERMINATION THE THERMAL EFFECTS OF HYDROTREATMENT OF COAL DISTILLATES

Abstract. Based on the data of the elemental constituents of the coal distillates and reaction products of the hydrotreating pre-defenolized feedstock in the presence of 5% Mo/Ni-Re catalyst, as well as the material balance of the production of diesel fuel components from fractions with a boiling point of 180-360 ° C the thermal effects were calculated. It was demonstrated that in the process of hydrotreating of coal distillates with boiling point at the range of 180-360 °C the values of thermal effects are 200-220 kJ/kg depending on the composition of the feedstock. The observed values of thermal effects of reactions of the hydrotreating of coal distillates with different fractional composition can be used for the designing of the appropriate processing units and for the construction of reactors. It also can be used for the evaluation of the chemistry reactions occurring during the hydrotreating of coal fractions depending on the nature of the catalytic reactivity of catalysts, as well as for the development of recommendations for using an effective catalyst.

Key words: coal distillates, diesel fuel, catalyst, thermal effect.

Introduction. One of the ways to increase the production of diesel fuels is to obtain them from the products of coal hydrogenation processing. Coal distillates contain considerable amount of heteroatomic compounds, unsaturated and aromatic hydrocarbons adversely affects the quality of motor fuels. For receiving stable components of diesel fuels with cetane rating not less than 45 it is necessary to provide sufficiently high degree of hydrogenation of phenols, nitrogenous bases, sulphur and unsaturated compounds, aromatic hydrocarbons contained in coal feedstock. [1-3].

In the course of technological design of the processes of coal distillate hydroforming the value of thermal effects of the reactions is of great importance. As a rule, during reactions with hydrogen absorption, a substantial amount of heat is produced (~125.4 kJ/mol of hydrogen that has entered into the reaction).

EXPERIMENTAL

Freshly distilled distillates with boiling point of 180-360 ℃ were used as a feedstock which was obtained by hydrogenation of brown coal from the Mamytsky deposit. Sulphur contained in the feedstock forms a part of nitrogen bases (quinoline, isoquinoline and their derivatives), oxygen forms a part of phenols (phenol, cresols, xylezols) [5].

Hydrotreating of feedstock and analysis of hydrogenisates was carried out in accordance with the methods [1,4,6]. 5 % Mo/Ni-Re was used as catalysts.

RESULTS AND DISCUSSION

In optimum conditions for the calculation of thermal effects, hydrogenation of coal distillates with boiling point up to 360 °C was conducted for the purpose of deriving a diesel fuel component from it.

It was found that if phenols and nitrogenous bases were previously removed from the feed, the volumetric flow rate of the process could be increased from 1.0 to 3.0 h^{-1} (table 1), while the degree of hydrogenation of unsaturated hydrocarbons was reduced: from 77.63 to 67,1 % and the degree of desulfurization – from 92.31 to 81.25 %.

Table 1 – Hydrotreating of dephenolized distillate with boiling point of 180-360 °C (400 ^{0}C, 6 MPa, 800 L of H_2/L of feedstock, 5 % of Mo/Ni-Re-catalyst)

Indicators	Initial feedstock	Characteristics of hydrogenate received at volumetric velocity, h^{-1}		
		2.0	2.5	3.0
Density, g/cm^3	0.8237	0.8542	0.8573	0.8580
Refractive index	1.4473	1.4783	1.4800	1.4809
Hydrocarbon compontents, wt. %:				
- unsaturated	7.6	1.6	2.3	2.5
- aromatic	36.6	29.5	29.3	29.3
- paraffins + naphthenes	80.8	89.7	88.7	88.5
Elemental composition, wt. %:				
C	87.12	87.24	87.58	87.52
H	12.22	12.68	12.32	12.36
S	0.64	0.08	0.10	0.12
N	0.02	missing	missing	missing

The hydrotreated product extracted under optimum conditions was distilled with fractions separated from the boiling point of 180 °C and from the boiling point of 180 °C-360 °C (a component of commercial diesel fuel).

Characteristics of the commercial diesel fuel component are shown in table 2 (Sample 1). Sample 1 contains 0.05 % of sulphur, less than 0.01 % of nitrogen. It should be noted that Sample 1 meets almost all the requirements of GOST 305-82 all-Union State Standard for "summer" diesel fuel with a cetane number of 45.

With the purpose of producing diesel fuel with higher Cetane number and lower setting point the total hydrotreated product was subjected to additional hydrogenation in order to reduce the content of aromatic hydrocarbons at the temperature of 250 0°C, pressure of 6 MPa, and the volume rate of 1.0 h^{-1} at the feed rate of 800 liters of H_2/l of feed over PdS/Al_2O_3 catalyst. The characteristics of the produced hydrogenate can be found in the table 3 and the characteristics of the diesel fuel component (Sample 2) in the table 2. Sample 2 meets almost all the requirements of the standard for "winter" diesel fuel with 49 Cetane.

Table 2 – The main physicochemical properties of diesel fuel components derived from coal hydrogenation products of the Mamytsky deposit

Indicators	Diesel fuel component	
	Sample 1 after hydrotreatment of the fraction with boiling point of 178-360 °C	Sample 2 after hydrogenation the aromatic hydrocarbons
Density at 20 °C, g/cm^3	0.8143	0.8423
Refractive index	1.4383	1.4655
Fraction, ˚C Initial BP 50 % is distilled at temperature 96 % is distilled at temperature End BP	 178 275 350 359	 177 260 338 351
Hydrocarbon compontents, wt. %: aromatic paraffins+naphthenes	 33.1 66.9	 21.0 79.0
Iodine number, g iodine per 100 g of fuel	3.7	missing
Content, % weight. Sulphur Nitrogen	 0.05 <0.01	 0.04 missing
Viscosity at 20 °C, cSt	5.1	5.0
Setting point, ˚C	-29	-35
Cloud point, ˚C	-7	-20
Resin , mg per 100 ml of fuel	14.0	5.0
Cetane number	45	49

Table 3 demonstrates the material balance of diesel fuel component production from coal distillate with boiling point 180-360 ^{0}C.

To determine the value of the thermal effects of typical hydrogenation reactions calculations for hydrotreating the fractions with boiling point of 180-360 ^{0}C have been made over tested catalysts on the basis of the data of elemental composition of feedstock and reaction products (table 2) and hydrotreating of preliminary dephenolized feedstock (Table 1), as well as material balance (table 3), according to the formula

$$-\Delta H = Q_s^r - Q_\text{B}^r \text{ (kJ/kg)} \quad (1)$$

where ΔH is the heat of product formation; Q_s^r is the heat of combustion of elements; Q_B^r is the highest calorific heat value. Thermal effect is defined as difference between the heats of formation of the final and the initial products.

Table 3 – Material balance of producing diesel fuel component from coal distillate with boiling point of 180-360 °C

Inflow	Weight, %	Outflow	Weight, %
Hydrotreating			
1. Coal distillate with boiling point at the range of 180-360 °C 2.Hydrogen for the reactions	100.0 1.9	Hydrogenate including: fraction with boiling point of 180 °C fraction with boiling point at the range of 180-360 ºC 2. Gas, including: C_1-C_3 H_2S NH_3 3. Water 4. Losses	97.3 7.8 89.5 2.0 1.0 0.7 0.3 2.2 0.5
Total	101.9		101.9
Hydration			
1. Hydrogenate 2. Hydrogen for the reactions	97.3 0.4	1. Hydrogenate 2. Losses	97.5 0.2
Total	97.7	Total	97.7
Distillation			
1. Hydrogenate	97.5	1. Fraction with boiling point 180 ºC 2. Fraction with boiling point at the range of 180-360 °C 3. Losses	13.9 83.4 0.2
Total	97.5	Total	97.5

Thermal effect of the reactions of hydrotreating of primary coal distillates with boiling point of 180-360 °C is 200-220 kJ/kg and it significantly decreases up to 41.8 kJ/kg during hydrotreating of preliminary dephenolized feedstock of the similar fractional composition, as due to removal of phenols from feedstock the hydrogen consumption for the process of water formation is significantly reduced.

For the 5 % Mo/Ni-Re catalyst the value of thermal effect of reactions is 200-220 kJ/kg, though an insignificant gas formation (3,7 %) is observed in its presence and selective hydrogenation of fractions with t.kip. 180-360 °C (yield of 45,5 % of the initial feedstock). The high heat of reactions in this case is determined by the fact that the 5 % Mo/Ni-Re catalyst in addition to the activation of hydrocracking reactions activates the reactions of hydrogenation of aromatic hydrocarbons (their content in hydrogenase decreases to 19.6 % in comparison with 65.4 % in the feedstock), which is accompanied by a high hydrogen consumption.

Conclusion. Consequently, as a matter of fact it can be concluded that in the course of hydrotreating of coal distillates with boiling point at the range of 180-360 °C the values of thermal effects are 200-220 kJ/kg, wich depend on the feed composition. The data of thermal effects of hydrotreating of coal distillates of different fractional composition can be used for design of appropriate processing units, and construction of reactors. It also can be used for evaluation the chemical properties of reactions occurring during hydrotreating of coal fractions depending on the nature of catalytic activity , as well as, for the development recommendations of using an effective catalyst.

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Резюме

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КӨМІР ДИСТИЛЛЯТТАРЫН ГИДРОБАЙЫТУ ҮРДІСІНДЕ ЖЫЛУ ЭФФЕКТІСІН АНЫҚТАУ

Шикізат және реакция өнімдерінің элементтік құрамы мен материалдық баланс мәліметтері негізінде қайнау температуралары 180-360 ^{0}C аралығында алынған көмір дистиллятының фракциялары және 5 % Mo/Ni-Re катализатор қатысында алдын ала фенолсыздандырылған шикізатты гидротазартудан алынған өнім үшін гидрлеу реакцияларының жылу эффектісі анықталынды. Алынған деректер негізінде қайнау температурасы 180-360°C болатын көмір дистилляттарын гидротазалау кезінде жылу эффектісінің шамасы шикізат құрамына қарай 200-220 кДж/кг болатындығы анықталынды. Анықталынған жылу эффектісінің мәндері тиісті технологиялық үрдістерді жобалауда және қажетті құрылғыларды таңдауда,, катализаторлардың активтілік сипатына қарай көмір фракцияларын гидробайыту барысындағы реакциялардың байыбын бағалау үшін пайдалануға болады.

Түйін сөздер: көмір дистилляттары, дизель отыны, катализатор, жылу эффектісі.

Резюме

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ОПРЕДЕЛЕНИЕ ТЕПЛОВЫХ ЭФФЕКТОВ
ГИДРООБЛАГОРАЖИВАНИЯ УГОЛЬНЫХ ДИСТИЛЛЯТОВ

Для определения величины тепловых эффектов типичных реакций гидрирования выполнены расчеты для гидроочистки фракций с т.кип. 180-360 ^{0}C в присутствии 5 % Mo/Ni-Re - катализатора на основании данных элементного состава сырья и продуктов реакций и по гидроочистке предварительно обесфеноленного сырья, а также материального баланса получения компонента дизельного топлива. Показано, что при гидроочистке угольных дистиллятов с т. кип. 180-360 °C величины тепловых эффектов соответствуют значениям 200-220 кДж/кг в зависимости от состава сырья. Полученные значения тепловых эффектов реакций процесса гидроочистки угольных дистиллятов различного фракционного состава могут быть использованы для проектирования соответствующих технологических аппаратов и конструирования реакционных устройств, оценки химизма реакций, протекающих при гидрооблагораживании угольных фракций в зависимости от характера каталитической активности катализаторов, а также для разработки рекомендаций по применению эффективного катализатора.

Ключевые слова: угольные дистилляты, дизельное топливо, катализатор, тепловой эффект.