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The Thermodynamic and Kinetic Characteristics of Adsorption Purification Process of Middle Distillate Fractions

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Abstract

There is a continuously increasing trend of producing ultra-clean diesel fuels with strict specifications of sulfur and polyaromatics. This is important to reduce the exhaust emissions such as sulfur oxides, nitrogen oxides, unburnt hydrocarbon compounds, and particulate matter. Therefore, thermodynamic and kinetic characteristics of adsorption methods at the middle distillate fraction from sulfur organic compounds were calculated. As a result, it`s established that adsorption methods may apply as an alternative method for the purification of middle distillates fractions obtained from primary refining from sulfur organic components.

Keywords: *Middle distillate fraction; Sulfur compounds; Adsorption; Gibbs energy.*

1. Introduction

The present paper aims to consider and calculate thermodynamic and kinetic characteristics of systems middle distillate fractions: selective adsorbents.

Desulfurization of liquid fuels is a challenging task for the refiners because of the undesirable effects of the sulfur compounds in petroleum, which hampers the refining operations and causes severe environmental degradation. The current worldwide stringent environmental regulations intensify more to produce liquid fuels with ultra-low levels of sulfur [1]. At present, catalytic hydrodesulphurization (HDS) is the sole process commercially used to desulfurize petroleum products. HDS is, however, an expensive process in terms of utilizing expensive operating conditions, i.e., high temperature, high pressure of hydrogen gas, and expensive catalyst, as well as it is inefficient to eliminate the sterically hindered sulfur compounds and thereby cannot achieve ultra-low levels of sulfur in the product fuels [2]. An alternative to the HDS process is desulfurization through adsorption, wherein sulfur compounds are selectively removed through adsorption on the solid adsorbent leaving behind sulfur-free fuel. However, the process is in the juvenile stage, and to be recognized as a commercially acceptable process, researchers are striving to increase its efficiency. A variety of adsorbents have been used for this purpose, such as modified composite oxides [3], activated carbon [4], mesoporous and microporous zeolites such as SBA-15, MCM-41 [5-7] 5-A, 13-X, ZSM-5, and Y-Zeolite. [8]. Other authors have also investigated the removal of sulfur compounds from crude petroleum, kerosene, and diesel oil by reactive adsorption using metal oxide; it was found that PbO_2 and MnO_2 were most effective in the desulfurization of all three fractions for 1 and 3 h reaction times in batch operation adsorption experiments [6].

To fully understand the nature of adsorption, the authors in [9-11] calculated the thermodynamic parameters associated with the adsorption process. They used equations that are based on the Van't Hoff equation, Langmuir constant to determine the change of the standard Gibbs free energy, standard enthalpy change, and standard entropy change.

2. Experimental

Samples of Bulgarian middle distillate fractions were used. The samples were characterized by determining their various physicochemical parameters, including gravity at 15°C, kinematic viscosity, aniline point, flash point, distillation characteristics, ash contents, Conradson carbon residue, water content, mechanical impurities, and total sulfur by employing the standard procedures of BSS and ASTM. The results from experimental physicochemical properties are presented in Table 1.

Table 1. Physicochemical properties of middle distillate fractions A1 and A2

Parameter	Method	Value A1	Value A2
Density at 15°C, g/cm^3	BSS EN ISO 3675	0.8310	0.8278
Flash point, °C	BSS EN ISO 2719	68	65.0
Kinematic viscosity at 40 °C, mm^2/s	BSS EN ISO 3104 + AC	2.84	2.52
Distillation characteristics, °C	BSS EN ISO 3405		
IBPC		188	187
10 %, °C		208	204
50 %,°C		252	242
90 %,°C		328	325
95 %,°C		355	348
FBP, °C		360	352
Sulfur content, %	BSS EN ISO 8754	0.1	0.082
Water content, % (v/v)	BSS ISO 3733	neal	neal
Mechanical impurities, %	St of CFMEA 2876	0.003	0.004
Ash content, % (m/m)	BSS EN ISO 6245	0.0006	0.0005
Pour point, °C	BSS ISO 3016	-14	-16
Coke residue, %	BSS EN ISO 10370	0.01	0.008
Polycyclic arene , %	BSS EN 12916	23.2	22.0

The adsorbents – silica gel and alumina, reagents and chemicals such as n-pentane, cyclohexane, and mixture from toluene and acetone (ratio 1:1) were with analytical grade. The detailed description and the equipment of the adsorption process are given in [12].

Before the alumina and silica gel were used for adsorption, they were modified with acids to remove the organic materials and increase adsorption capacity. First, the samples were modified with a solution of hydrochloric acid. Next, 50 g of the alumina or silica gel samples were taken in the round-bottomed flask, and 250 mL of the 0.1 N solution of hydrochloric acid was added to them and refluxed for 2 h. The alumina or silica gel slurry was then filtered through vacuum filtration and washed with an excess of double-distilled water. The samples were then dried in the oven at 105±2°C for 5 h. Finally, the alumina or silica gel samples were activated by heating at 450-550°C in the muffle furnace for 4 h and stored in vacuum desiccators.

After activation of the adsorbents, the latter were placed in the adsorption column and sealed by tapping with a rubber stopper. Filling the column for the individual experiments with silica gel and alumina, respectively, was performed by the dry method. After loading the column, 15 g of the test gas oil component, previously dissolved in three times the solvent n-pentane, was poured into it. The weight ratio of the investigated gas oil components to the input adsorbent was 1:20. The collection rate of the individual filtrates was about 10 cm^3/min, depending on the duration of the individual adsorption processes and the amount of eluent. The eluents were fed successively in the following order: n-pentane, cyclohexane, and mixture from toluene and acetone (ratio 1:1).

The individual fractions were collected in pre-weighed beaker cups, the solvent was evaporated on a water bath, and the resulting residue was weighed to a constant mass.

The residues of arenes were determined on the residues thus obtained by the standardized method of aniline points and the sulfur content, according to BSS ISO 8754. The obtained results are reflected in [13].

The activation thermodynamic and kinetic parameters were calculated in the equations according to the transition theory. The obtained experimental data are given in Tables from 2 to 9.

Table 2. Thermodynamic characteristics of the system raw material A1: Silica gel ratio A1: Silica gel = 1:20

T, K	τ, h	ΔH, kJ/mol	ΔS, kJ/mol	ΔG, kJ/mol
293,15	1,0	-2286,30	11,50	-7107,10
293,15	1,5	-2286,30	9,88	-6380,21
293,15	2,0	-2286,30	7,04	-4190,10
293,15	3,0	-2286,30	5,40	-4050,25
293,15	4,5	-2286,30	4,60	-3845,11
293,15	6,0	-2286,30	3,64	-3568,60
303,15	1,0	-2354,60	8,55	-5218,34
303,15	1,5	-2519,36	7,09	-4668,14
303,15	2,0	-2519,36	4,87	-3996,04
303,15	3,0	-2519,36	3,98	-3726,38
303,15	4,5	-2519,36	1,93	-3104,09
303,15	6,0	-2519,36	1,48	-2968,98
313,15	1,0	-2602,54	6,90	-4762,45
313,15	1,5	-2602,54	5,18	-4225,24
313,15	2,0	-2602,54	3,28	-3628,28
313,15	3,0	-2602,54	2,33	-3333,70
313,15	4,5	-2602,54	0,83	-2862,21
313,15	6,0	-2602,54	-0,70	-2384,04
323,15	1,0	-2685,71	5,80	-4558,93
323,15	1,5	-2685,71	3,95	-3963,08
323,15	2,0	-2685,71	2,61	-3529,74
323,15	3,0	-2685,71	1,93	-3309,14
323,15	4,5	-2685,71	0,01	-2689,97
323,15	6,0	-2685,71	-1,18	-2305,44

Table 3. Thermodynamic characteristics of the system raw material A1: alumina ratio A1: alumina = 1:20

T, K	τ, h	ΔH, kJ/mol	ΔS, kJ/mol.K	ΔG, kJ/mol
293,15	1,0	-862,10	-1,78	-450,24
293,15	1,5	-1102,11	-3,63	-1105,45
293,15	2,0	-4457,76	-7,58	-2568,80
293,15	3,0	-6865,40	-11,58	-3551,62
293,15	4,5	-8111,70	-14,01	-4125,68
293,15	6,0	-9232,43	-16,10	-4764,54
303,15	1,0	-1643,23	-3,58	-764,35
303,15	1,5	-2640,20	-6,55	-1620,80
303,15	2,0	-5107,16	-8,37	-2764,43
303,15	3,0	-6668,78	-11,56	-3426,68
303,15	4,5	-8815,35	-14,55	-4545,33
303,15	6,0	10915,58	-18,32	-5554,58
313,15	1,0	-4810,18	-7,89	-2514,45
313,15	1,5			
313,15	2,0	-6110,70	-9,63	-3215,20
313,15	3,0	-8680,60	-13,60	-4470,65
313,15	4,5	-9515,60	-14,89	-4777,15
313,15	6,0	-11016,20	-16,88	-5651,50
323,15	1,0	-3632,90	-5,71	-1810,40
323,15	1,5	6343,34	-10,22	-3381,15
323,15	2,0	-6433,90	-11,80	-3662,37
323,15	3,0	-9108,75	-14,06	-4610,40
323,15	4,5	-10998,32	-16,44	-5534,64
323,15	6,0	-11664,75	-18,25	-5761,14

Table 4. Thermodynamic characteristics of the system raw material A2: Silica gel ratio A2: Silica gel = 1:20

T, K	τ, h	ΔH, kJ/mol	ΔS, kJ/mol	ΔG, kJ/mol
293,15	1,0	-2717,60	12,65	-6632,40
293,15	1,5	-2717,60	11,15	-5410,23
293,15	2,0	-2717,60	7,24	-4625,44
293,15	3,0	-2717,60	5,88	-4460,13
293,15	4,5	-2717,60	5,25	-4011,54
293,15	6,0	-2717,60	4,27	-3869,20
303,15	1,0	-2620,72	9,18	-5332,24
303,15	1,5	-2620,72	8,16	-4870,34
303,15	2,0	-2620,72	5,56	-4114,28
303,15	3,0	-2620,72	4,01	-4057,11
303,15	4,5	-2620,72	2,22	-3417,19
303,15	6,0	-2812,26	1,93	-3044,26
313,15	1,0	-2812,26	7,33	-4877,74
313,15	1,5	-2812,26	5,66	-4662,60
313,15	2,0	-2812,26	3,55	-3717,44
313,15	3,0	-2812,26	2,78	-3666,80
313,15	4,5	-2812,26	0,99	-2919,34
313,15	6,0	-2812,26	-1,11	-2515,16
323,15	1,0	-2715,18	5,14	-4704,34
323,15	1,5	-2715,18	4,01	-4111,17
323,15	2,0	-2715,18	3,22	-3737,48
323,15	3,0	-2715,18	2,52	-3665,51
323,15	4,5	-2715,18	0,05	-2889,30
323,15	6,0	-2715,18	-1,33	-2564,88

Table 5. Thermodynamic characteristics of the system raw material A2: alumina ratio A2: alumina = 1:20

T, K	τ, h	ΔH, kJ/mol	ΔS, kJ/mol.K	ΔG, kJ/mol
293,15	1,0	-1010,16	-2,11	-481,60
293,15	1,5	-2225,10	-4,46	-1110,34
293,15	2,0	-4444,89	-8,61	-2346,80
293,15	3,0	-6880,00	-12,12	-3644,55
293,15	4,5	-8105,76	-14,44	-4440,68
293,15	6,0	-9336,30	-16,78	-4844,35
303,15	1,0	-1684,37	-2,78	-844,40
303,15	1,5	-2662,67	-5,15	-1325,90
303,15	2,0	-5264,75	-9,24	-2616,14
303,15	3,0	-6668,99	-11,48	-3641,13
303,15	4,5	-8868,26	-15,10	-4144,10
303,15	6,0	-1101,45	-18,60	-5481,78
313,15	1,0	-2274,80	-3,89	-1145,20
313,15	1,5	-4998.87	-8,54	-2417,65
313,15	2,0	- 6110,60	-10,15	-3110,32
313,15	3,0	-8666,80	-14,10	-4440,40
313,15	4,5	-9331,30	-15,60	-4775,12
313,15	6,0	-10661,23	-17,10	-6016,65
323,15	1,0	-3661,05	-6,60	-1830,43
323,15	1,5	-6561,64	-10,01	-3110,09
323,15	2,0	-7220.90	-11,07	-3603,30
323,15	3,0	-9011,10	-14,20	-4661,60
323,15	4,5	-10664,60	-17,13	-5344,54
323,15	6,0	-11666,70	-18,41	-6012.15

Table 6. Kinetic characteristics of system middle distillate fraction A1: Silica gel = 1:20

T, K	Reaction constant, s^{-1}	Activation energy (E_a), kJ/mol	Arrhenius constant
293,15	225,12	0,9545	588558,10
303,15	363,20	0,9255	588558,10
313,15	470,08	0,9018	588558,10
323,15	474,10	0,8983	588558,10

Table 7. Kinetic characteristics of system middle distillate fraction A1: alumina = 1:20

T, K	Reaction constant, s^{-1}	Activation energy (E_a), kJ/mol	Arrhenius constant
293,15	393,26	0,7314	111347,40
303,15	393,26	0,7117	111347,40
313,15	555,14	0,7015	111347,40
323,15	663,09	0,7004	111347,40

Table 8. Kinetic characteristics of system middle distillate fraction A2: Silica gel = 1:20

T, K	Reaction constant, s^{-1}	Activation energy (E_a), kJ/mol	Arrhenius constant
293,15	266,10	1,2151	1810116
303,15	398,40	1,1064	1810116
313,15	498,32	1,0151	1810116
323,15	555,34	0,9925	1810116

Table 9. Kinetic characteristics of system middle distillate fraction A2: alumina = 1:20

T, K	Reaction constant, s^{-1}	Activation energy (E_a), kJ/mol	Arrhenius constant
293,15	444.45	0,6335	71184,46
303,15	466,17	0,6125	71184,46
313,15	593,89	0,6013	71184,46
323,15	711,88	0,5886	71184,46

3. Results and discussion

The obtained results in tables presented the calculated thermodynamic and kinetic characteristics of specific raw material systems: selective adsorbent.

As shown by the calculated data obtained at all temperatures we studied, the duration of contact and the ratio of raw material: adsorbent purification process is thermodynamically possible. It should be noted that with increasing temperature, contact time, and raw material: adsorbent ratio, we get better results for Gibbs energy and entropy. The best results are obtained using adsorbent alumina and raw material in the ratio = 20: 1, other things being equal. Intermediate values are obtained using an adsorbent of silica gel in a ratio of 20: 1 with the same other conditions. The negative values obtained for the free energy (Gibbs energy) confirm the experimental data for the adsorption process of the raw materials we studied while showing that this process is thermodynamically possible for all the systems we studied.

From the obtained data on the entropy of the distribution of the individual systems, it can be seen that in the process of adsorption of the middle distillates fractions studied by us, the most probable interaction of the type of specific solvation is performed, without noticeable thermal effect.

4. Conclusions

It has been proven that we get better results for Gibbs energy and entropy with increasing temperature and contact time. The best results are obtained using adsorbent alumina and the investigated middle distillate raw material A1 at a ratio = 20:1. Intermediate results are obtained with adsorbents silica gel and alumina with investigated raw materials A1and A2 ratio: 20:1.

The negative values obtained for the free energy confirmed the experimental data for the adsorption process of the raw materials we studied while showing that this process is spontaneous and thermodynamically possible for all adsorption systems we studied.

From the obtained data on the entropy of the distribution of the individual systems, it can be seen that in the process of adsorption of the studied middle distillate fractions with the selected adsorbents, most likely an interaction of the specific solvation type is performed, without noticeable thermal effect.

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