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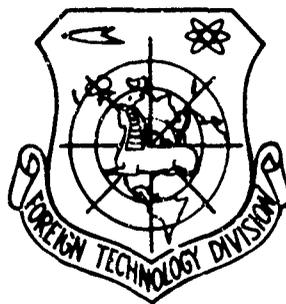
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DESULFURIZATION AND REFINING OF GASOLINE AND JET FUEL BY
MEANS OF SURFACE-ACTIVE AGENTS IN A FLUIDIZED BED

By

K. Werner



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**DESULFURIZATION AND REFINING OF GASOLINE AND JET FUEL BY MEANS
OF SURFACE-ACTIVE AGENTS IN A FLUIDIZED BED**

By K. Werner

("Walter Ulbricht" Leuna Plant, Leuna, German Democratic Republic)

Submitted 24 March, 1962¹

The hydrocarbon compounds contained in petroleum are, according to origin, adulterated with compounds containing sulfur, oxygen, and nitrogen. Due to the corrosive effect of these substances, as well as to the unpleasant odor and the poor storage stability of unrefined gasoline, problems connected with refining have already been under study for a long time. Up to the end of World War II, technical refining was to a predominant extent carried out via treatment with chemical agents. Due to the relatively high price of hydrogen, the already known hydrofining process could make headway against these selective refining processes only at a very slow pace. Only since the technical introduction of the hydrogen-producing reforming process have

these procedures constituted an integral part of modern refining technique. However, already today trends are becoming discernable which indicate that the quantities of hydrogen being delivered by means of the reforming process are no longer sufficient for hydrofining in the future. This circumstance comes about due to the fact that constantly higher requirements are being set for the degree of refinement also of the fractions above the boiling range of diesel oil, and, furthermore, with the introduction of the hydrocracking process there appears an additional vehicle of demand for hydrogen. It is therefore of immediate importance that for low-boiling fractions attempts should be made to develop refining processes which operate without hydrogen consumption. A report shall be given here concerning the results of our research in this field.

The known sweetening processes are excluded for our purposes, since they reduce the total sulfur content of the initial product only to an insubstantial extent. On the other hand, considerable desulfurization takes place in the case of the adsorption processes, which for this reason were subjected to closer examination as non-hydrogen-consuming refining procedures. Within the scope of the present paper it is unfortunately impossible to go into greater detail concerning theoretical considerations. To characterize the selected adsorption system, reference is made only to the thermodynamic equilibria of some sulfur compounds (see Fig. 1) in the boiling range of gasoline.²

The decomposition of sulfur compounds into olefins and H_2S takes place most advantageously within the range of 300 - 400° C and higher, in the course whereof particularly light mercaptans are thermally cracked. If, furthermore, the conclusions from the works of Langmuir, Freundlich, as well as Brunauer, Emmett, and Teller are taken into account, consideration should be given, for the refining of light hydrocarbons, to a process in a gaseous-solid two-phase system with utilization of the fluidized-bed principle. In the course thereof, both the adsorption and the regeneration should be carried out in the fluidized bed, spent adsorbent being constantly drawn

out of the reactor. In the regenerator connected on the outlet side, the regeneration would have to take place continuously at correspondingly higher temperatures. The activated, highly heated adsorbent then proceeds anew into the reactor. By means of this manner of operation, a constant, relatively little-spent state of the adsorbent is guaranteed in the reactor. Besides this, it is possible to work with a high circulation ratio, i.e., with a large excess of regenerated adsorbent in relation to the input of raw material.

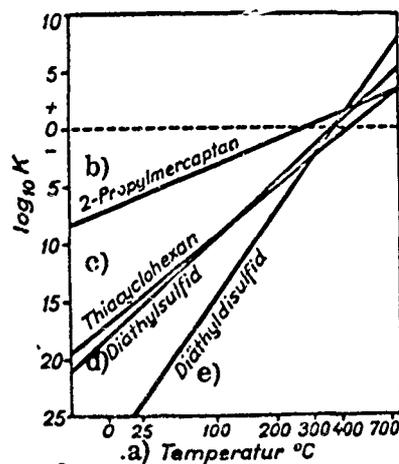


Fig. 1. Decomposition of sulfur compounds.

CODE: a) Temperature; b) 2 - pro
pylmercaptan; c) thiacyclohexane;
d) diethyl sulfide; e) diethyl di-
sulfide.

After the direction in which the work was to proceed had been established, investigations were first of all carried out with various adsorbents in a test apparatus developed for this purpose (Figure 2).

The vaporized hydrocarbons entered the reactor at the bottom end and streamed toward a quasifluid layer which was maintained by means of mechanical agitation. The adsorbent mixture to be tested was fed through the reactor in a counterstream. It was possible to test 30 adsorbent mixtures in this apparatus. Various types of silica gel, active and crude alumina and bauxite were used as components; these were in part

activated by iron or other metals. Of the numerous test series some typical results shall be given (Table I).

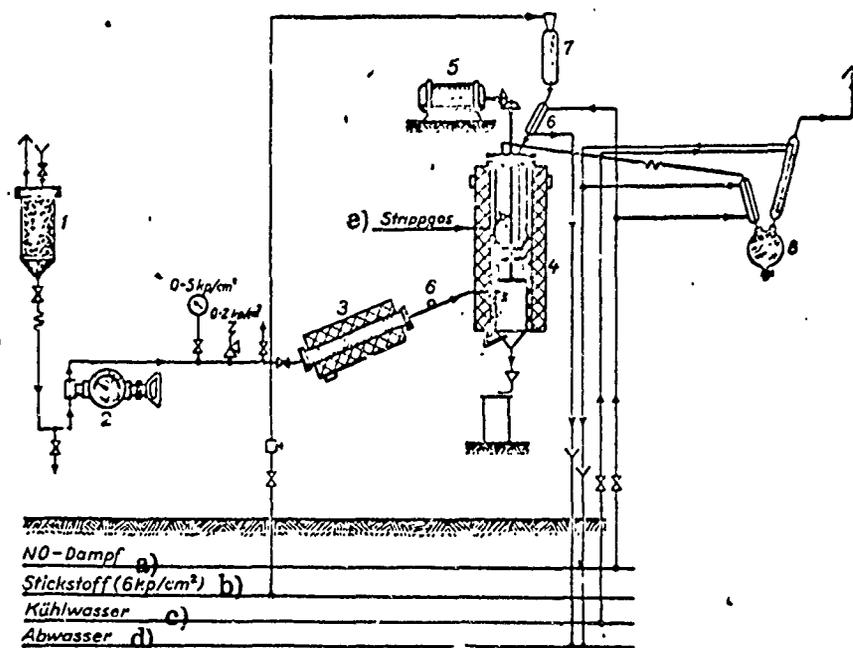


Fig. 2. Schematic diagram of apparatus with tested solid layer.

CODE: a) No vapor; b) nitrogen (6 kp/cm²); c) cooling water; d) waste water; e) stripped gas.

Although silica gel possesses the greatest surface, the degree of desulfurization was nevertheless perceptibly below that of the adsorbent mixtures containing iron oxide. Among the selected reaction conditions, H₂S occurred obviously as a dissociation product of the mercaptans, e. g., 2-propylmercaptan (boiling point 68° C). In accordance with expectations, the iron content of the adsorbent has virtually no effect on the content of bases in the yield product. In order to better characterize the refining of phenols and bases, a light-oil-containing gasoline, produced by means of the joint processing of lignite low-temperature carbonization products and Soviet petroleum, was used as an input product (Table II).

Due to the quantitative removal of bases as well as an almost complete separation of phenols, the originally dark and malodorous input products came out clear as water

and odorless. Again it can be seen from the table that the iron content influences only the degree of desulfurization. Furthermore it is interesting that in contrast to hydrofining, due to their great dipole moments, the base and phenol components are substantially easier to remove than are sulfur compounds.

Table I
Refining of Romashkino straight-run distillate 240° C with silica gel-alumina-iron oxide mixture at 332° C.

a) Nr.	b) Adsorptionsmittel- zusammensetzung	c) Schwefel, in Gew.-%			Basen in mg NH ₂ /g	
		d) Einsatz- produkt	e) Anfall- produkt	f) Entschwefelungs- grad	h) Einsatz- produkt	i) Anfall- produkt
A 1	Silicagel, Typ A .j).....	0,11	0,027	75%	1,8	0,5
A 2	A-Gel + 10% Roh-tonerde .k).	0,11	0,22	80%	1,8	0,4
A 4	A-Gel + 10% Roh-tonerde + + 4,5% Fe ₂ O ₃l).....	0,11	0,012		1,8	0,4
A 5	A-Gel + 5% Fe ₂ O ₃ ..m)....	0,11	0,011	90%	1,8	0,1

Note: Commas represent decimal points.

CODE: a) No. ; b) composition of adsorbent; c) sulfur, % by weight; d) product; e) yield product; f) degree of desulfurization; g) bases in mg NH₂/1; h) input product; i) yield product; j) silica gel, type A; k) A-gel + 10% crude alumina; l) A-gel + 10% crude alumina + 4.5% Fe₂O₃; m) A-gel + 5% Fe₂O₃;

Table II
Elimination of bases and phenols from A-gasoline with a silica gel-alumina-iron oxide mixture.

a) Nr.	b) Adsorptionsmittel- zusammensetzung	c) Basen in mg NH ₂ /l		d) Phenole, Gew.-%			f) Entschwefelungs- grad
		e) Ein- satz- produkt	g) Raffi- nat	h) Ein- satz- produkt	i) Raffinat	j) Raffinierungs- grad.	
S 1	Silicagel, Typ S k).....	360	0,0	0,15	0,013	97%	31,5%
S 4	S-Gel + 1% Fe ₂ O ₃l).....	360	0,0	0,15	0,012	98%	66,6%
S 2	S-Gel + 9,5% Tonerde + + 0,5% Fe ₂ O ₃m)....	360	0,0	0,15	0,004	99,1%	92,3%
S 3	S-Gel + 2,5% Fe ₂ O ₃ + + 47,5% Tonerden).....	360	0,0	0,15	0,003	99,2%	75%

Note: Commas represent decimal points.

CODE: a) No. ; b) composition of adsorbent; c) bases in mg NH₂/1; d) input product; e) refined product; f) phenols, % by weight; g) input product; h) refined product; i) degree of refinement; j) degree of desulfurization; k) silica gel, type S; l) s-gel + 1% Fe₂O₃; m) s-gel + 9.5% alumina + 0.5% Fe₂O₃; n) s-gel + 2.5% Fe₂O₃ + 47.5% alumina.

In the further course of the work, investigations were carried out concerning the replacement of the heretofore described mixtures of synthetic adsorbents by cheaper products. The results of some experiments are summarized in Table III.

It was possible to obtain particularly favorable desulfurization effects with a solidified Hungarian bauxite as well as with a Jugoslavian crude bauxite. This effect was of the same order of magnitude as in the case of the substantially more expensive silica gel- Fe_2O_3 -alumina mixtures. The same favorable effects with regard to the elimination of phenols and bases could also be established with the use of A-gasoline.

The investigations hitherto carried out in the quasifluidized-bed installation confirm the usefulness of adsorptive refining for low-boiling mineral-oil fractions. Optimum process parameters were found at which an effective and cheap adsorbent produced very good elimination of bases and phenols as well as sufficient separation of sulfur. To substantiate the hitherto obtained experimental results, it would be necessary for the principle of adsorptive refining to be verified in a true fluid manner of operation in a combined adsorption-regeneration system. Figure 3 shows a diagram of the experimental equipment developed for this purpose.

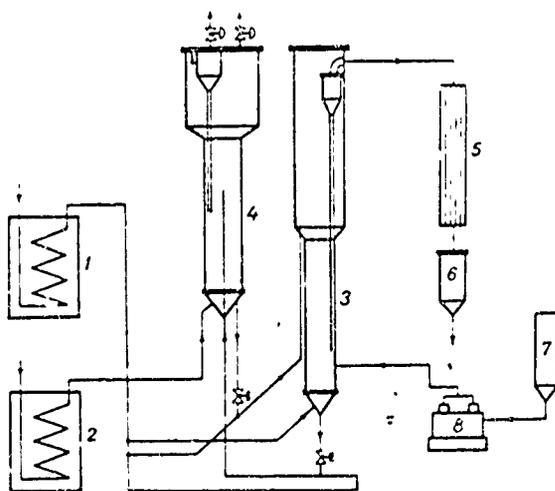


Fig. 3. Schematic diagram of the small scale fluidized-layer installation.

The most important parts of the installation are the reactor (3), made of sichromal steel, and the regenerator (2). The actual reaction space in the reactor has a diameter of 150 mm and a length of 2000 mm. To prevent the removal of dust, a plenum chamber as well as a dust cyclone were located above the reactor. Fluidization was effected in the reactor by means of the vaporized input product or by means of hot nitrogen. In the regenerator, fluidization was effected by means of preheated air. The adsorbent could be continuously drawn from the reactor and from the regenerator, through siphons regulated by means of a special gate valve and could be delivered pneumatically to the regenerator or the reactor by means of preheated nitrogen. The height of the fluidized bed in the regenerator and in the reactor was controlled by means of differential measurements. The same principle was used to determine the quantities of circulating solids. The pressure difference between the reactor and the generator was automatically controlled. Due to lack of time, it is impossible to go into the numerous experiences that were encountered in the course of work with this equipment. It can only be said that after initial difficulties, it was possible to achieve troublefree operation of this experimental equipment.

The first experiments in this equipment served to verify the findings obtained in the small installation. A solidified Hungarian bauxite with a grain size of 0.06 - 0.5 mm was used as adsorbent. The texture analysis of this product will be gone into later. Regeneration of the used-up adsorbent was effected by means of oxidation by air at 510°C. The spent state of adsorbent could be observed very well due to the onset of a color difference.

Figure 4 depicts the effect of the load, the adsorption temperature, and the conditions of circulation on sulfur separation. Each of the analyses was made on the basis of 4-hour balance experiments.

The temperature dependence of the sulfur decomposition is determined by two factors, namely the absolute adsorption capacity of the bauxite and the thermal

decomposition of the sulfur compounds, particularly of the mercaptans. For this reason, above 332° the degree of desulfurization diminishes constantly due to a reduction of the adsorption capacity. The maximum at 332° must be ascribed to a preferred thermal decomposition of the sulfur compounds into H₂S and olefins. This determination is in agreement with the thermodynamic relationships shown in Figure 1. As expected, at a constant absolute circulation of solids the sulfur decomposition diminishes as the amount injected increases. Here loads within the limits of 0.47 to 1.25 kg/kg/h were being dealt with. The sulfur separation diminished from 84% to 69%. The third curve shows the sulfur separation in relation to the circulation ratio, adsorbent circulation of 20 - 160 kg/h being dealt with here. The rise of the degree of desulfurization as the adsorbent circulation increases, i. e., as the period spent by the adsorbent in the reactor diminishes, and with the diminution of the spent state connected therewith, corresponds to the theoretical expectations. The drop of this curve at solid circulations above 100 kg/h was due to shortcomings of the equipment. Under these conditions it was impossible to attain sufficient regeneration due to short periods spent in the regenerator.

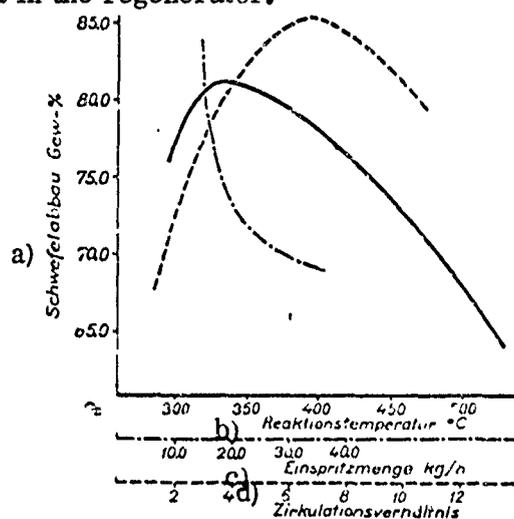


Fig. 4. Sulfur separation.

CODE: a) sulfur separation % by weight;
 b) reaction temperature; c) amount injected; d) circulation ratio.

After studying the effect of various reaction parameters it was necessary, in a prolonged experiment, to study yield conditions and changes of the adsorbent in the case of long adsorption-regeneration cycles. Romashkino straight-run gasoline with a boiling end point of 200° was used as the input product. The findings are presented in Table IV.

Table III
Refining of Romashkino straight-run gasoline (SE 240°C) with mixtures of alumina, Fe₂O₃, and bauxite.

a) Nr.	b) Adsorptionsmittel- zusammensetzung	c) Schwefel in Gew.-%			g) Basen in mg NH ₃ /g	
		d) Einsatz- produkt	e) Raffinat	f) Entschwefelungsgrad	h) Einsatz- produkt	i) Raffinat
T 1	95% Rohtonerde + 5% Fe ₂ O ₃ (j)	0,11	0,02	82%	2,4	0,0
T 2	50% Rohtonerde + 50% La- masse k).....	0,11	0,05	56%	2,4	0,6
T 3	verfestigter ungar. Bauxit (l)	0,11	0,009	92%	2,4	0,1
T 5	jugosl. Bauxit m)...	0,11	0,013	87%	2,4	0,0
T 7	T 3 mit Wasserstoff aktiviert (n)	0,11	0,013	87%	2,4	0,0

Note: Commas represent decimal points.

CODE: a) No. ; b) composition of adsorbent; c) sulfur, in % by weight; d) input product; e) refined product; f) degree of desulfurization; g) bases in mg NH₃/l; h) input product; i) refined product; j) 95% crude alumina + 5% Fe₂O₃; k) 50% crude alumina + 50% refined material; l) solidified Hungarian bauxite; m) Yugoslavian bauxite; n) T 3 activated with hydrogen.

Table VI
15-day experiment in the refining of Romashkino straight-run gasoline.

Einsatzmenge a)	Zirkulationsverhältnis d)	Einsatz- produkt b)	Anfangsprodukt c)		
			30 kg/h	30 kg/h	40 kg/h
			4,5 : 1	2,7 : 1	2,0 : 1
dj°		0,741	0,746	0,746	0,745
Bromzahl, g/100 g e).....		1,1	1,0	1,0	1,0
Schwefelgehalt, Gew.-% f).....		0,053	0,011	0,012	0,013
Schwefelabbau, Gew.-% g).....		—	79,2	77,4	75,4
Ausbeute, Gew.-% h).....		—	97,9	98,4	98,5

Note: Commas represent decimal points.

CODE: a) Amount injected; b) input product; c) yield product; d) circulation ratio; e) bromide number, g/100 g; f) sulfur content, % by weight; g) sulfur separation, % by weight; h) yield, % by weight.

It was possible to conduct the prolonged experiment uninterruptedly over a period of 15 days without any difficulty.

During this period about 10 tons of crude gasoline were refined. The residual sulfur content in the refined product permits the gasoline to be further processed in reforming installations. The yields were relatively high, although an additional increase appears still possible through improved channeling of stripped gas. Through comparative investigations of the texture analysis of the adsorbent after various running times, it could be proved that no essential changes appeared in the adsorbent during the experiment (Table V).

Table V

Texture analyses of the employed adsorbent in relation to the operating time.

a) Texturdaten	Probenehme nach b)					
	0	144	168	216	336	384
	Stunden Dauerbetrieb c)					
Scheinbare Dichte, g/cm ³ d)	1,74	1,75	1,75	1,74	1,78	1,80
Wahre Dichte, g/cm ³ .. e)	3,15	3,18	3,20	3,16	3,25	3,21
Kornvolumen, cm ³ /g .. f)	0,575	0,571	0,571	0,575	0,562	0,555
Gerüstvolumen, cm ³ /g .. g)	0,317	0,314	0,312	0,316	0,307	0,311
Gesamthohlraumvolumen, h) cm ³ /g	0,258	0,257	0,259	0,259	0,255	0,244
Mikroporenvolumen, cm ³ /g i)	0,228	0,236	0,235	0,239	0,215	0,204
Makroporenvolumen, cm ³ /g j)	0,030	0,021	0,024	0,020	0,040	0,040
Porosität, %	44,95	45,01	45,36	45,04	45,37	43,96
Oberfläche, m ² /g	86,6	91,7	88,0	90,0	81,8	81,5

Note: Commas represent decimal points.

CODE: a) Texture data b) Sample taken after c) Hours of continuous operation; d) apparent density g/cm³; e) true density, g/cm³; f) grain volume, cm³/g; g) skeleton volume, cm³/g; h) total void volume, cm³/g; i) micropore volume, cm³/g; j) macropore volume, cm³/g; k) porosity, %; l) surface, m²/g.

The trifling reduction of the surface of the adsorbent must be attributed to change in the grain-size distribution. The same statement applies also to the insignificant change in the micropore volume.

It is consequently possible to prove by means of the prolonged experiment that with regard to sulfur separation and adsorption capacity, no substantial changes in sulfur separation are to be expected even in case of the extended operation of a

combined fluid-adsorption-regeneration process.

For the sake of completeness, a brief report shall also be made concerning two experimental series carried out with other input products. This concerns a jet fuel made according to Soviet formulas from Romashkino petroleum fractions. These refining experiments dealt above all with removal of the so-called "active sulfur component." The results are presented in Table VI.

The degree of desulfurization was in the expected range. Cracking of pure hydrocarbons did not occur, as can be seen from the course of the bromine number, the density, and the aniline point. It can, however, not be seen from Table VI that in the course of the approx. 73% desulfurization, the active sulfur was nearly quantitatively removed. To characterize this statement, the input product and the refined product were investigated by means of a high-sensitivity copper-strip test according to Annable and Haines. Here a standardized copper strip was brought into contact with the substance to be tested not, as customary, at 50°C, but at boiling temperature. After the sample was distilled off, the color condition of the copper strip provided evidence concerning the content of corrosive sulfur components.

The unwashed refined product from the adsorption refining had a negative high-sensitivity copper-strip test and, accordingly, an activated-sulfur content of under 0.004 % by weight.

In a closing, a few short notes concerning the refining of a pyrolysis gasoline fraction. Due to the thermal instability of this product, a multistage hydrofining process, requiring a very large outlay of equipment, is required for it. The possibility was investigated of so altering this product by means of adsorptive refining that it could be subsequently processed in a standard hydrofining installation under classical conditions. A pyrolysis gasoline from the Most Chemical Plant was used as the input product. It had a bromine number of 56 and a glass-dish test of 542 mg/100 ml. The operating conditions in the pilot installation were

reaction temperature	325°C
load in reactor	0.1 - 0.36 kg/kg/h
regeneration temperature	550°C
circulation ratio	5 ~ 8:1

Table VI

Refining of turbine fuel from Romashkino crude oil.

Reaction conditions:		Regeneration conditions:	
amount injected	30 kg/h	regeneration temperature	510°
reaction temperature	332°	amount of air	9.1 Nm ³ /h
load	0.9 kg/kg/h	circulation ratio	3:1

Analytische Daten	a)	Einatzprodukt b)	Raffinat c)
d ₄ ²⁰		0.785	0.784
Bromzahl, g/100 g. d)		4.5	3.5
Anilinpunkt	e)	58.9	58.3
Schwefelgehalt, Gew.-% f)		0.24	0.065
Schwefelabbau, Gew.-% g)		—	72.9
Basengehalt, mg NH ₃ /l h)		2.4	nicht nachweisbar
Phenolgehalt, Gew.-% i)		0.033	nicht nachweisbar
Ausbeute, % j)		—	99

CODE: a) Analytical data; b) input product; c) refined product; d) bromine number; e) aniline point; f) sulfur content % by weight; g) sulfur separation, % by weight; h) base content mg NH₃/l; i) phenol content, % by weight; j) yield %; k) not detectable.

The liquid yield was 90 %. In terms of BTX aromatics it was nevertheless almost 100. The obtained product had a bromine number of only 15-20 units and a glass-dish test of about 20 mg/100 ml.

By means of similar investigations with small-small equipment it was possible to prove, on the basis of the constancy of the glass-dish test of the refined product after oxygen treatment under pressure, that the luminary refined products obtained in this manner manifest sufficient thermal stability. Consequently, subsequent processing in a classical medium-pressure hydrofining installation appears to be possible. Final statements can, of course, be made only after these investigations have been completely concluded.

To conclude the proceedings, I should also like to take this opportunity to express my gratitude to my colleagues, Messrs. Dipl. -Chem. Seidel, Dipl. -Chem. Hey and Chemical Engineer Voekler, for their outstanding contribution in solving the numerous scientific and technical problems of this project.

SUMMARY

Investigations with regard to the simultaneous removal of S, O, and N compounds from low-boiling hydrocarbons by means of treatment with surface-active agents are reported on. It is shown that the application of fluidization techniques results in considerable advantages over other known processes. The experiments were carried out without the use of additional hydrogen at temperatures above the boiling temperatures of the feed fractions.

A great variety of adsorbents and adsorbents mixtures was tested. It was found that the phenolic and basic components could be removed with considerably greater ease than in the known medium-pressure refining processes. Desulfurization amounted to approximately 80% in the experiments, which were conducted under normal pressure, the so-called aggressive sulfur compounds, in their turn, being removed almost quantitatively.

In conclusion, a report is given on the development of a continuous pilot plant for about 20 kg feed/hour, which is operated according to the principles of fluidization both in its refining and regeneration sections. Experimental results from this plant are given.

FOOTNOTES

- p. 1 ¹Delivered as a lecture at the Petroleum Conference, Budapest, April, 1962.
p. 2 ²Compare Rossin et al.: Selected Values of Physical and Thermodynamical Properties of Hydrocarbons.

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