The Hydrocracking of Egyptian Heavy Residual Fuel Oils[*]

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Dedicated to Professor August Guyer

Summary

The hydrocracking of straight-run residual fuel oils obtained from heavy egyptian crudes was investigated. A recently developed process, using a molybdenum- and cobalt-containing catalyst, has shown significant advantages over the established Varga process: The advantages observed reside in better middle distillates' yields, lower reaction pressure and one stage operation. A processing scheme based on hydrocracking appears to be the most attractive alternative which may be applied to adapt yield distribution of products obtainable from heavy egyptian crude oils to the local market requirements.

1. Introduction

The great majority of crude oils produced from oil fields discovered in the United Arab Republic-Egypt prior to 1960 are of the sour heavy type. Table 1 compiles the most significant characteristics of some of these crudes, as compared to the imported russian and arabian crude oils, while Table 2 gives the yields of marketable straight-run products obtainable from a few typical crudes listed in Table 1. A characteristic feature common to all egyptian crude oils mentioned is the low gasoline content and the practical absence of middle distillates.[**] A study of the Middle-East (including the United Arab Republic) and European market situation reveals that the general trend of processing crude oils should be directed towards minimizing gasoline yields,

Table 2. Marketable straight run products obtainable from some U.A.R. oils (% weight)

Products	Gharib	Matamer	Balayim	Arabian	Russian
Gases	1.19	0.43	0.87	0.99	1.33
L.P.G.	0.61	0.22	0.18	1.36	0.85
Gasoline	8.93	1.55	6.72	13.23	15.45
Kerosene	5.56	–	–	17.90	10.02
Gasoil	2.78	–	–	10.40	13.08
Diesel oil	3.51	–	–	4.26	4.43
Residual fuel oil	74.73	95.42	89.85	49.45	52.42
Sulfur	0.28	–	–	–	–
Losses	2.41	2.38	2.38	2.41	2.42
Total	100.00	100.00	100.00	100.00	100.00

Table 1. Main characteristics of representative crude oils produced in the U.A.R.-Egypt prior to 1960

Characteristics	Gharib	Matamer	Balayim	Bakr	Karim	Arabian	Russian
Specific gravity 15/4°C	0.9035	0.9488	0.9328	0.9350	0.9530	0.854	0.860
Sulphur content, % weight	2.85	2.55	2.8	4.6	4	1.6	1.45
Water content, % volume	0.55	0.6	0.23	0.15	0.2	0.05	0.25
Salt content, % weight	0.007	0.008	0.2	0.012	0.005	0.002	0.005
Pour point, °F	25	20	34	34	42	< 20 °F	< 20 °F
Sediments, % weight	0.02	0.02	0.01	0.01	0.02	absent	absent
Conradson carbon, % weight	8.6	9.9	12.3	10.8	14.4	3.4	3.35
Ash content, % weight	0.028	–	0.06	0.035	0.013	0.02	0.02
Viscosity Red 1 at 100°F (seconds)	125	1150	450	940	3035	37	40
Reid V.P. at 100°F (psig.)	4	0.1	–	2.8	2.4	–	6
Distillation:							
I. B. P., °C	65	–	65	68	68	53	53.5
% volume recovered at 100°C	3.5	–	5	3.5	3	8	12.0
% ,, ,, ,, 125°C	7.0	–	7	8.0	5	14	18.0
% ,, ,, ,, 150°C	11.0	–	11	12.0	8	20	26.0
% ,, ,, ,, 175°C	15.0	1	14	14.0	10	26	32.0
% ,, ,, ,, 200°C	19.0	3	17	16.0	12	31	37.0
% ,, ,, ,, 225°C	23.0	6	20	21.0	15	36	42.0
% ,, ,, ,, 250°C	27.0	9	22	26.5	17	41	46.5
% ,, ,, ,, 275°C	31.0	11.5	25	28.0	20	46	52.0
% ,, ,, ,, 300°C	35.0	11.5	33	35.0	25	52	56.0

[*] Received March 28, 1967.

[**] The newly discovered fields of Marine Balayim, Morgan and El Alamain are producing high API gravity oils, containing distillate products in amounts and qualities comparable to the arabian or Kuwait crude oils.

Table 3. Annual yields of products obtained from processing Balayim residue by the delayed coking process

		Tons/year
Feed		
Balayim residue		1,700,000
Asphaltic and waxy residues (from lube manufacturing process)		105,600
Full range naphtha		486,000
	Total	2,291,600
Products		
Gasoline O. N. 100		290,000
Kerosene		578,000
Gasoil		275,000
Diesel oil		189,000
Fuel oil		82,400
Propane (L. P. G.)		46,200
Butane (L. P. G.)		42,300
Light hydrocarbon gases		70,800
Light gasoline (raw material for Petrochemicals)		120,000
Naphtha (reforming feedstock)		86,000
Sulphur		28,200
Coke		382,000
Benzene		3,000
Dodecyl benzene		6,000
Losses and unaccounted for		92,700
	Total	2,291,600

while increasing middle distillates and light fuel production to the maximum possible. To achieve this goal, either of two alternative processing schemes may be adopted: Bottoms from conventional distillation units are further fed to either a coker or a hydrocracker.

Attention was especially focused on the Balayim oil field,[1] which was discovered in 1955 on the Sinai-Peninsula, 210 km south of Suez, because production rates from this particular field exceed by far those from other fields. Prior to 1965, Land Balayim crude oil was processed in the U. A. R. by conventional atmospheric distillation, to produce 92% residual fuel oil and 8% gasoline. As part of a scheme to adapt product yields to the local market consumption figures, a delayed coking unit was put into operation in 1965 for the further processing of Balayim residual fuel at the rate of 1,700,000 tons/year. The coker complex, comprising catalytic reforming, hydro-desulphurization and sulphur recovery facilities, produces a variety of products which are listed in Table 3; the important yield of middle distillates is the most attractive feature of the process. The only disadvantage of such a processing scheme lies in the production of coke with high sulphur content to such an extent, that its utilization is often connected with serious difficulties. This is why it was thought of hydrocracking, as a possible improvement of the adopted processing trend.

The purpose of this investigation is therefore to evaluate hydrocracking as a means of increasing the proportion of middle distillate products obtainable from Land Balayim crude oil.

2. Upgrading Land Balayim fuel oil by the Varga hydrocracking process

Destructive hydrogenation of coal tar and heavy residual fuel oils was already a common practice in the early twenties of our century, after Dr. PIER of the BASF in Germany had developed the preliminary experiments of Professor BERGIUS (1913) into an industrial process. The pressures prevailing in the reactor, at that time, were in the range between 200 and 1000 atmospheres, which is considered as a serious disadvantage. Recent improvements were introduced in 1956 by Professor VARGA in Hungary and the first true hydrocracking process, called the Varga process, uses an iron oxide catalyst on a coal carrier and is operated at a relatively moderate pressure.[2,3] It is beyond the scope of our report to give a detailed description of the latter process.

In 1962, a pilot scale investigation was carried out at the «Institute for high pressure techniques» in Hungary on the hydrocracking of Balayim, Bakr and Karim crude oils by the Varga process. We will limit our report to the experiments on Balayim crude. Liquid phase hydrocracking of this crude oil was carried out in a two liter reactor at a pressure of 70 kg/cm^2, a temperature of

Table 4. Main characteristics of Land Balayim crude oil

Tests	Results
Specific gravity 25/4 °C	0.9289
Asphaltenes, % weight	9.5
Sulfur content, % weight	3.13
Salt content, % weight	–
Distillates % volume	
Boiling range I. B. P.–180 °C	10.0
,, ,, 180–350 °C	19.5
,, ,, 350–400 °C	8.6
,, ,, 400–500 °C	13.8
,, ,, > 500 °C	47.2
Losses	0.9
Characteristics of fractions	
I. Gasoline fraction (I. B. P. to 180 °C)	
Specific gravity 25/4 °C	0.7361
Sulphur content, % weight	0.13
II. Diesel oil (180 to 350 °C)	
Specific gravity 25/4 °C	0.8373
Sulphur contents, % weight	1.72
Pour point, °C	19.5
III. Fraction (350 to 400 °C)	
Specific gravity 25/4 °C	0.8911
Sulphur content, % weight	2.68
Pour point, °C	18
IV. Fraction 400 to 500 °C	
Specific gravity 25/4 °C	0.9230
Sulphur content, % weight	2.56
V. Fraction boiling above 500 °C	
Specific gravity 25/4 °C	1.061
Sulphur content, % weight	4.31

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[1] *Petroleum 23* (1960) 224–9.

[2] J. VARGA, GY. RABO and A. SZEKELY, *Acta Chem. Acad. Sci. Hung. 5* (1955) 433–51.

[3] J. VARGA, J. KAROLYI, GY. RABO, P. STEINGAGZNER, A. SZEKELY and A. ZALAI, *Petroleum Refiner 36* (1957) fasc. 9.

443 °C and a volumetric space velocity of 1.01 kg/liter/hour. The characteristics of the Balayim crude oil[4] fed to the reactor are given in Table 4, while Table 5 compiles yields and significant qualities of the products obtained.* Reported results show that the Varga hydrocracking process, if compared to straight run fractionation, does not increase gasoline yield significantly, while it increases diesel fuel output (180 to 350 °C cut) to approximately twice its original value, on the expense of the residue boiling above 500 °C.

Table 5. Yields and qualities of products obtained from the hydrocracking of Land Balayim crude oil by the Varga process

Feed	*% weight*
Balayim crude oil	100
Catalyst	7.7
Hydrogen	0.6
	108.3

Products	Boiling range	% weight	Inspection
1. *Gasoline*	I.B.P.–180 °C	9.7	
Specific gravity 20/4 °C			0.785
Sulphur % weight			0.1
O.N. (motor) + 4 cm³ TEL			70.8
2. *Diesel Oil*	180–350 °C	38.6	
Specific gravity 20/4 °C			0.845
Sulphur, % weight			0.2
Pour point, °C			– 19
Centane number			46
3. *Light Fuel oil*	350–400 °C	13.3	
Specific gravity 20/4 °C			0.881
Sulphur, % weight			0.5
Pour point, °C			20
Engler viscosity at 50 °C, degrees			1.7
4. *Heavy fuel oil*	400–500 °C	15.2	
Specific gravity 50/4 °C			0.920
Sulphur, % weight			1.9
Pour point, °C			35
5. *Residue*	above 500 °C	25.5	
Specific gravity 50/4 °C			1.18
Solids (including catalyst), % weight			18–22
6. *Gases and losses*		6.0	
Total		108.3	

3. The hydrocracking of Land Balayim residue using molybdenum and cobalt containing catalysts

Since 1950, extensive research has been carried out in the U.S.S.R., at the Academy of Science, under the supervision of Y. R. Katsobashvili, on the hydrocracking of residual fuel oils at low pressures (10 to 30 atm). Within the framework of this research plan, experiments were performed on Land Balayim residue. Because of its high viscosity and its excessive asphaltenes and resins content, which would cause a rapid deactivation of the catalyst,[5] the Balayim fuel oil had to be admixed with 33,3% by weight of a distillate fraction as diluent; the properties of fuel oil and diluent are given in Table 6.

Table 6. Properties of residue and diluent subjected to hydrocracking

Parameters	Residue	Diluent
Specific gravity 20/4 °C	0.9827	0.8165
Sulphur, % weight	3.8	1.24
Asphaltenes, % weight	17.5	–
Conradson carbon, % weight	17.0	–
Distillation		
I.B.P. °C	250	200
Recovery up to 200 °C volume %	–	–
,, ,, ,, 250 °C ,,	1.0	100
,, ,, ,, 300 °C ,,	5.0	–
,, ,, ,, 350 °C ,,	12.5	–
,, ,, ,, 400 °C ,,	20.0	–
,, ,, ,, 450 °C ,,	28.5	–
,, ,, ,, 500 °C ,,	40.0	–
Fraction boiling above 500 °C volume %	60.0	–

Fig. 1 represents a flow diagramm of the test apparatus.

A brief outline of the experimental procedure follows: The reactor, having a total volume of 500 cm³, was filled with 300 cm³ fresh catalyst (grain size: 2 mm). After circulating

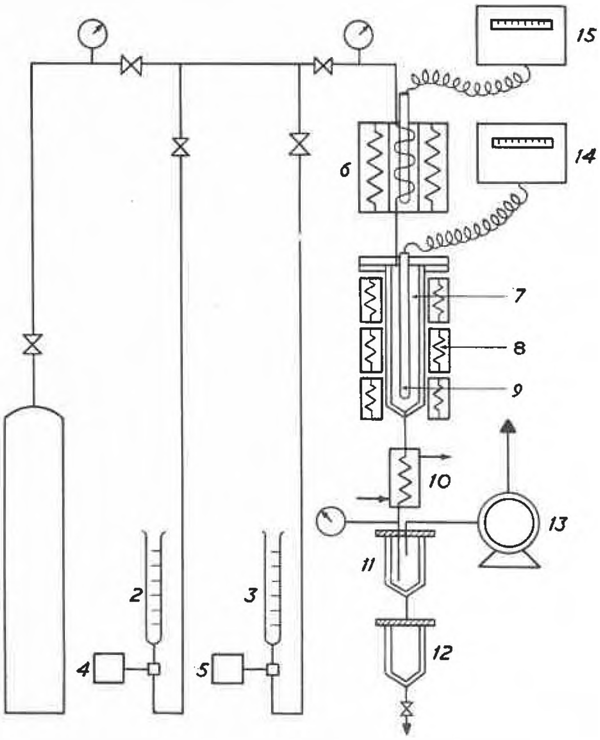

Fig. 1. Simplified flow diagram of hydrocracking pilot unit (test equipment). 1 Hydrogen container, 2 Feed burette, 3 Water burette, 4 Feed pump, 5 Displacement water pump, 6 Preheater, 7 Reactor, 8 Reactor heater, 9 Thermocouple well, 10 Cooler, 11 High pressure separator, 12 Low pressure separator, 13 Flow meter for gaseous products, 14 and 15 Temperature recorders

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* Private communication.

[4] *Petroleum 19* (1956) 273–6.

[5] Y. R. Katsobashvili and N. S. Korkoba, *Petroleum Inst. Bull. Acad. Sci U.S.S.R. 6* (1955) fasc. 10.

Table 7. Hydrocracking of Land Balayim residue

	Test numbers							
	1	2	3	4	5	6	7	8
I. *Conditions of tests*								
Type of catalyst	A	A	A	A	A	A	A	B
Temperature, °C	460	480	430	510	480	460	480	480
Pressure, kg/cm^2	30	30	30	30	30	30	30	30
Volumetric space velocity, kg. liter^{-1}. hour^{-1}	1.80	1.80	1.74	2.74	2.70	2.40	2.62	1.80
Hydrogen feed rate liter/kg liq. feed (at N.T.P.)	885	877	765	1131	1021	1023	1178	976
II. *Products output*								
Gas and losses, % weight	13.0	14.15	12.25	20.07	15.52	13.5	15.61	12.82
Liquid hydrocracked product, % weight	80.5	77.5	84.4	70.0	78.0	82.0	79.0	80.0
Coke, % weight	6.5	8.35	3.35	9.93	6.48	4.5	5.39	7.18
III. *Characteristics of liquid hydrocracked product:*								
Density	0.843	0.836	0.858	0.827	0.848	0.843	0.846	0.835
Sulphur content, % weight	0.54	0.42	1.00	0.33	0.82	1.00	0.85	0.51
Iodine number	8	14	6	20	12	8	10	6
Asphaltenes, % weight	0.26	0.27	1.53	0.19	0.91	0.31	0.42	0.49
Fractions output, % weight								
I.B.P. to 200°C	14.0	24.5	10.0	39.5	17.5	13.0	17.5	20.0
200–300°C	46.0	40.0	46.5	26.5	38.5	45.0	35.0	37.0
300–350°C	9.8	11.3	9.0	15.0	12.5	10.0	9.5	11.8
350–500°C	29.0	22.5	24.5	18.5	26.8	24.0	29.5	25.0
Residue Boiling above 500°C	1.2	1.7	10.0	0.5	4.7	8.0	8.5	6.2

hydrogen through the system during thirty minutes, under the same conditions of pressure and temperature set for the experiment, the preheated feed, together with the hydrogen was introduced at a constant rate into the reactor. The quantitative recovery of products from the system was achieved by displacement, in such a way, that water was pumped through the catalyst bed, maintaining the experiment's pressure and temperature levels. The effluent from the reactor was cooled and separated in a two stage separator into a vapour- and a liquid-phase.

Eight experiments were carried out, for the purpose of studying the effects of temperature, volumetric space velocity, hydrogen-to-feed ratio and type of catalyst on the yields (Table 7) and qualities (Table 8) of the products. A discussion of the results obtained is given below:

a) *Effect of temperature:* Experiments 1 to 4 show that a rise in reaction temperature, while maintaining

Table 8. Characteristics of fractions obtained from the hydrocracked liquid product

	Tests numbers							
	1	2	3	4	5	6	7	8
I. *Gasoline fraction I.B.P. –200°C*	0.753	0.746	0.762	0.765	0.761	0.761	0.753	0.755
Specific gravity 20/4°C								
Sulphur, % weight	0.20	0.12	0.25	0.05	0.15	0.15	0.21	0.09
Iodine number	22.6	14.0	26.7	18.1	35.9	40.1	35.3	24.5
Octane number (motor)	61	53	51	58	51	59	53	57
II. *Fraction 200–300°C*								
Specific gravity 20/4°C	0.827	0.832	0.823	0.825	0.821	0.821	0.822	0.825
Sulphur, % weight	0.61	0.57	0.64	0.26	0.53	0.77	0.56	0.35
Iodine number	4.0	4.6	6	2.4	2.2	3.2	4.1	3.6
Sulphonated matter, % volume	31.7	36.7	31.8	11.7	23.2	35.4	32.8	38.9
III. *Fraction 300–350°C*								
Specific gravity 20/4°C	0.975	0.880	0.869	0.899	0.863	0.863	0.862	0.859
Sulphur, % weight	1.14	1.07	1.32	0.80	1.04	1.31	1.22	0.77
IV. *Fraction 350–500°C*								
Specific gravity 20/4°C	0.913	0.907	0.913	0.911	0.912	0.905	0.908	0.903
Sulphur, % weight	0.97	0.90	1.49	0.93	1.53	1.60	1.04	0.70
V. *Residue boiling above 500°C*								
Specific gravity 20/4°C	0.956	0.998	1.031	1.021	1.054	0.988	1.009	0.997
Sulphur, % weight	1.18	0.89	2.06	1.21	1.56	1.80	2.25	2.02

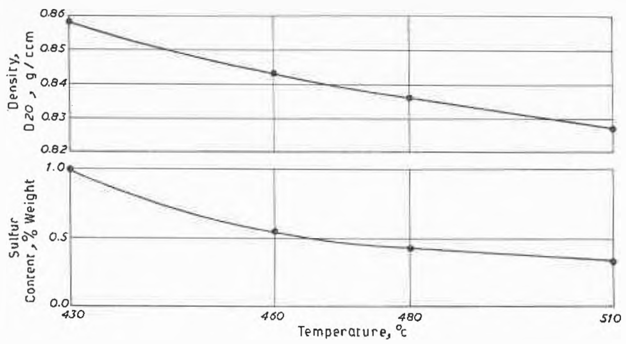

Fig. 2. The effect of temperature on the properties of the liquid product obtained from hydrocracking Land Balayim residual fuel oil (Volumetric space velocity: 1.8 kg/liter/hour)

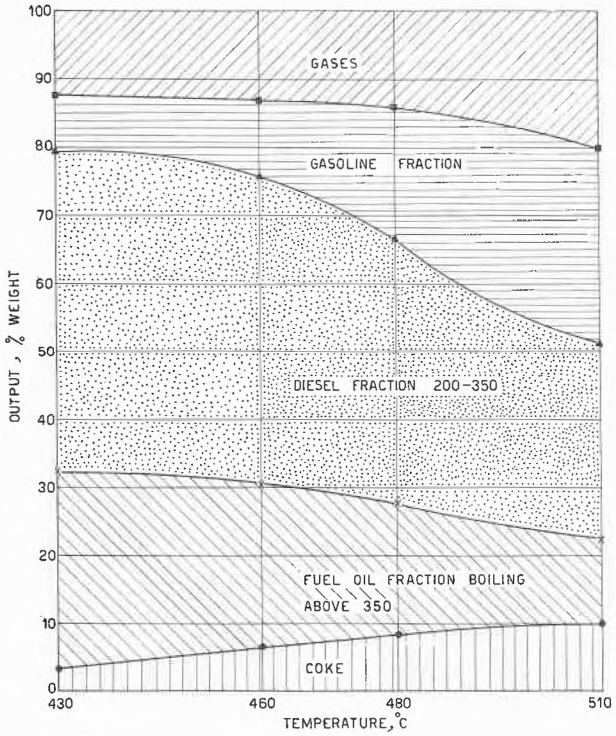

Fig. 3. The effect of temperature on the distribution of the hydrocracked products – Material balance (Volumetric space velocity: 1.8 kg/liter/hour)

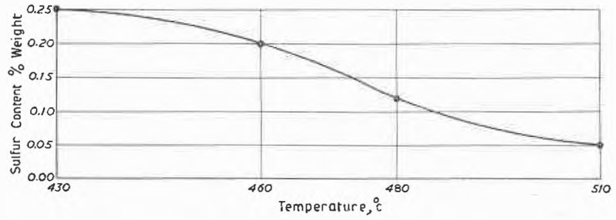

Fig. 4. The effect of temperature on the sulphur content of the gasoline fraction obtained form hydrocracking Land Balayim residual fuel oil

space velocity at a constant value of 1.8 kg/liter/hour, is accompanied by a lower density and a lower sulphur content of the products (Fig. 2), higher gasoline, gases and coke yields and a decreased total liquid distillates production (Fig. 3), because of increased hydrocracking severity. At 510 °C, a complete conversion of the feed into fractions boiling below 500 °C is attained. The sulphur content of the gasoline fraction is significantly reduced by an increase in temperature (Fig. 4).

b) *Effect of volumetric space velocity:* A higher space velocity means a reduced residence time and, consequently, a reduced hydrocracking severity. Therefore, as long as severity is set below conditions for maximum gasoline yield, raising space velocity from 1.80 to 2.70 kg/liter/hour and thus reducing time of reaction, manifests itself in a lower gasoline yield and a reduced output of gaseous products.

c) *Effect of catalyst:* Experiments 1 to 7 were carried out using an alumina-molybdena-catalyst (type A) which consists of 14% by weight of MoO_3 on an Al_2O_3 carrier. The catalyst used in experiment 8 (type B) contains 12% MoO_3 and 8% CoO precipitated on Al_2O_3.

A comparison between the sulphur content figures of the various products obtained in experiments 2 and 8 (Table 8), reveals that catalyst B, containing Cobalt, is superior especially as far as desulphurization is concerned.

4. On the production of marketable products by the described hydrocracking process

The graphical plot of the material balance (Fig. 3) indicates that the described process can be operated to produce either gasoline or middle distillates as main products. The fraction 200 to 350 °C, obtained under the various operating conditions, conforms to the U.A.R. local requirements for summer diesel fuel with respect to its sulphur content. The residue boiling above 350 °C is suitable as fuel oil blending component.

The gasoline fractions obtained from all tests, with the exception of 4 and 8, show a low Octane Number (motor) of 55 and a sulphur content higher than the permissible maximum limit of 0.1%. The production of a marketable gasoline necessitates further processing in a catalytic reforming unit. The low O.N. indicates that the catalysts employed are mainly hydrogenating catalysts and do not favour aromatization or isomerization.

5. Conclusive remarks

The hydrocracking of Land Balayim residual fuel in the liquid phase, using Molybdenum and Cobalt containing catalysts (type B), yields (experiment 8) 12% catalytic reforming feedstock, 43% diesel oil, 25% fuel oil, 7% coke and gases which may be utilized for hydrogen production. It is worthwhile mentioning that better yields are usually obtained when processing is carried out on the industrial scale and especially if a fluid or moving catalyst bed is used.[6] Furthermore, the described process shows significant advantages over the Varga process, i. e. lower reaction pressure, one stage operation, deeper desulphurization and higher output of middle distillates.

Based on the investigational results reported, an alternative processing scheme including hydrocracking may be applied with advantage to upgrading Land Balayim and similar heavy crude oils.

Acknowledgement: The Authors wish to thank Professor Dr. Y. L. Gorevitch of the Moscow Petroleum Institute, for his valuable assistance in carrying out this investigation.

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[6] M. Chervenak, C. Johnson and S. Schuman, *Petroleum Refiner 39* (1960) fasc. 10, p. 151–65.