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TRANSLATION

HIGH PRESSURE HYDROGENATION OF HEAVY PETROLEUM DISTILLATES

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V. Mraz, O. Krafft and R. Kubicka

Summary

Favourable processes of treatment of heavy petroleum distillates in a hydrogenation plant are disclosed, viz. the high pressure hydrorefining and the high pressure hydrocracking at 300 at.

The hydrogenation products formed in the high pressure hydrorefining are very good raw materials for producing high quality lubricating oil, as well as light paraffin and ceresine products.

By means of high pressure hydrocracking, either motor fuel can be obtained as main product, or the heavy distillate can be converted into diesel oil by means of the selective catalysts developed recently. A high grade jet fuel can also be obtained in this process. The two process methods mentioned involve a considerably more favourable utilisation of the imported sulphur-containing paraffinic crude.

HIGH PRESSURE HYDROGENATION OF HEAVY PETROLEUM DISTILLATES

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Utilization of refined products obtained from sulphurous, paraffin-based crude oil was thoroughly studied and developed. Hydrogenation of these distillates is known and was thoroughly introduced in practical application. However, this is not the case with heavy petroleum distillates which have to be produced by means of vacuum distillation.

A hydrogenation plant which originally was intended for processing tars at 300 atmospheres absolute pressure and presently for the most part processes paraffin-based, sulphurous crude oil would be especially interested in the development of now economical and technological high pressure hydrogenation processes for intermediate petroleum products. It is known that refined petroleum products can easily be desulphurized at high pressure, however, an undesirable superhydrogenation occurs whereby aromatic substances convert to naphthenes, thus causing excessive hydrogen consumption. Medium pressure hydrogenation is therefore de-

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sirable

Proper utilization of a high pressure hydrogenation plant brings about high pressure hydrogenation of vacuum distillates (paraffin oils).

Hydrogenation of lubricant materials is not new and can be carried out at various strict conditions. The mildest of the employed hydrogenation processes (1-12) are carried out at temperatures ranging from 250 to 350°C and at 40 to 60 atmospheres absolute pressure. Practically 100% product exploitation is attained at a consumption of 4 to 45 liters hydrogen per 1 liter of processed oil. The objective of the hydrogenation involved is the finishing of oil product and it replaces the generally utilized hot contact refining. Only 10 to 25% desulphurization is attained in this process.

If reaction temperature is increased to 380 - 400°C then the degree of desulphurization is increased to 80 - 99% (13-17). Great changes can be observed in the composition of hydrogenated oils. 10 - 15% gasoline and Diesel oil are produced by means of cracking. The viscosity index is increased.

High pressure hydrogenation at 300 atmospheres absolute pressure can be recommended for hydrogenation plants. This high pressure method was thus far applied mainly in the ČSSR (13, 18, 19, 20) and the Soviet Union (15, 16). Work is carried out under conditions similar to high pressure hydrorefining of petroleum and tar distillates. Attainable desulphurization: 85 - 99%. Considerable changes are achieved in the composition of hydrogenated products. Chemical changes in oils can be regulated by the choice of catalysts and reaction conditions. Formation of light components (Diesel oil and gasoline) is higher and amounts to 15 - 30%. Hydrogen consumption is approximately 220 Nm^3 per 1 t. It is not necessary to subject to selective refining products of high pressure hydrogenation, however, occasional mild after-treatment is recommended. In addition to motor oils, white paraffin and ceresin as well as turbine oils can be produced from high pressure hydrogenation products. The application of high pressure hydrogenation in oil distillates therefore offers better utilization of paraffin-based and sulphurous crude oil. Extensive results obtained by us in this field will be published by Večerka and Schnabel in a special publication (20). It is also our intention to report in detail about an additional suitable process of exploiting a high pressure hydrogenation plant for oil distillates, i.e. concerning its high pressure hydrocracking process. According to our experience, high pressure in contrast to medium pressure has certain important advantages in the hydrocracking process.

Hydrocracking of petroleum distillates had a characteristic development. The first stage concerns the production of so-called synthetic fuels by means of high pressure hydrogenation and makes reference to the hydrogenation of tars and coals including crude oil residues and hydrogenated distillates (18, 21, 22, 23, 24).

The development of thermal and especially modern catalytic cracking processes overshadows the importance of the aforementioned hydrocracking process.

During the past 10 years, interest in hydrocracking of crude oil distillates and residues increased considerably. Closely interrelated is the development of the reformed gasoline process which represents a source of cheap hydrogen residue (25, 26). The following processes were developed for hydrocracking of residues: GULF HDS (33), H-Oil (34, 35), KAZOBASCHVILI (36, 37, 38); the VARGA process (39, 40, 41) and others (24, 32) take advantage of the favorable influence exercised on dilution of raw material residue by a lighter product. Similar to the known high pressure petroleum distillation of medium distillates are the following modern medium pressure hydrocracking processes: Isocracking (27, 28, 29). Unicracking (30, 31), Lomax (32). Processed are medium distillates (gas oils) of various origin. The raw material is either prehydrogenated (isocracking) or the process is completed in two stages, the first stage have a refining function.

We have determined that high pressure plants working at 300 atmospheres absolute pressure have the advantage that they are able to process, without preliminary treatment, heavy vacuum crude oil distillates.

New formation of Diesel oil in the cracking of oils is more desireous for CSSR requirements than formation of gasoline.

We were able to ascertain that the composition of heavy crude oil distillates cracked by hydrogenation can be influenced by the catalyst and that the following products can be obtained under various conditions: gasoline, Diesel oil, and jet fuel. Production of these fuels can be increased without increasing the amount of crude oil and the quality of produced fuels, particularly jet fuels and Diesel oils can be improved and the amount of heating oil can be reduced.

We also investigated the cracking of vacuum distillates as obtained from the Muchanovo and Romaschinko crude oil or their mixtures without preliminary treatment by distillates. Hydrorefining and actual cracking can be combined into a single technological process. Table I contains technical data on the hydrocracking process when using two types of catalysts. The cracking process can be influenced in favor of gasoline or Diesel oil by choosing a suitable cracking catalyst.

Table I

Hydrocracking of Paraffin Oils from Muchanovo Crude Oil to Gasoline (Catalyst A) and Diesel Oil (Catalyst B)

Conditions for reaction	Hydrogenation with catalyst A	Hydrogenation with catalyst B
Pressure	300 atm.absol.press.	300atm.absol. press.
Partial pressure, H_2	190 " " "	190 atm.absol. press.
Temperature, °C	440-450°C	460°
Space Velocity	0.4 1/1 h	0.8 1/1 h
Gas-Product Ratio	2,000 N 1/1	1,500 N 1/1
Exploitation of liquid product, weight-%	80	95

Analysis	Raw Material	Hydrogenation Remover A	Hydrogenation Remover B
Density/20°C	0.900	0.770	0.788
Dist. Curve boiling point, °C	320.	53.	70.
to 200°C Vol.-%	—	55.	39.
to 325°C Vol.-%	6.5	86.5	83.
to 360°C Vol.-%	15.	90.	94.
End of boiling	approx. 500°C	approx. 400°C	approx. 400°C
Viscosity/50°C	3.5 E		
Sulphur content, weight-%	1.70	0.02	0.02
Phenols, mg/l	100.	10.	5.
Bases, mg/l (as NH_3)	150.	1.	0.7
Element. C weight-%	85.85	85.43	85.82
Anal. H weight-%	12.55	14.53	14.26

The catalyst designated with "A" is produced on the basis of activated earth and the catalyst designated with "B" on the basis of argillaceous earth. Both catalysts contained metals in the form of sulfides of the VI and VIII group. A higher yield of liquid hydrocracking products were obtained when using catalyst "B". Hydrogen consumption is also lower as compared to the cracking process employing catalyst "A" and gasoline. In gasoline cracking with catalyst "A", hydrogen consumption is approximately 430 Nm^3/t injection product, in Diesel oil cracking with catalyst "B" approximately 320 Nm3/t injection product. The quality of gasoline, Diesel oil and jet fuels obtained through distillation from the remover of the hydrocracking process and involving catalysts "A" and "B", is recorded in table II-IV.

Table II

Quality of Gasolines Obtained from Hydrocracking Removers

	Catalyst A	Catalyst B
(Fraction to 160°C)		
Yield in reference to hydrogenation remover	37.5	15.6
Density at 20°C	0.730	0.741
Boiling point	60°C	71°C
5%	71°C	86°C
50%	105°C	123°C

95%	153 °C	153 °C
End of boiling	163/98	162/98
Aromatic substances and olefine, weight %	15.9	3.1
Naphthene, weight %	34.7	46.6
Paraffins, weight %	49.4	50.3
Sulphur content, weight %	0.003	0.004

The influence of reaction temperature on the distillate composition is evident from fig. 1. Reaction temperatures of 440-460° are suitable for hydrocracking.

Date in table I reveal that it was possible to simultaneously eliminate the phenols and bases when engaging in hydrocracking of paraffin oils. Phenols in the amount of up to 1,000 mg/l and bases in the amount of up to 700 mg/l exercised no influence on the hydrocracking process. No decrease in activity of the mentioned catalyst could be determined even in long-duration tests with such raw materials (up to 2,000 h). After hydrogenation experiments, the carbon content in the catalyst amounted to maximum 6.5%, similar to other catalysts in preliminary hydrogenation and petroleum distillation of tar and crude oil raw materials.

Catalyst "B", which for selective cracking of oil distillates was overwhelmingly developed to Diesel oil, also possesses excellent refining capability. This characteristic of the catalyst is not essentially influenced at higher temperatures by a preceded cracking period as to customary in common refining contacts. This is evident from experimental results with a mixture injection product of tar and crude oil (table V).

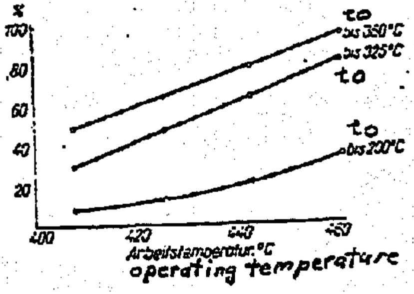

Figure 1. Selective hydrocracking of heavy crude oil distillates to Diesel oil exploitation of fractions to 200, 325, and 360° in dependence of temperature.

Higher yield of refined products is noticeable when applying paraffin oil hydrocracking to a technological plan of crude oil processing. Processing of Muchanovo crude oil yields approximately 20% and Romaschkino crude oil approximately 25% paraffin oil. In cracking the entire amount, aimed directly at the production of Diesel oil and jet fuel fractions, the following can be obtained calculated on the basis of crude oil:

gasoline	[illegible]
jet fuel	10.5%
Diesel oil over 240°C	11%

The quality of jet fuel obtained from the hydrocracked product is better than what the GOST 7149-54 standard specifies for TS 1 fuel; the qualitative reserve even corresponds to the T - 1 GOST 4138-49 standard. Therefore, inferior quality jet fuel obtained from paraffinic crude oil by means of primary distillation can be improved by this product. The quality of jet fuel processed from Muchanovo crude oil and hydrocracked strippers involving the use of both catalysts is recorded in table III.

Table III

Quality of Jet Fuel Fractions 130 - 240°C, of Hydrogenation Removers A and B and a Similar Primary Fraction from Muchanovo Crude Oil.

	Catalyst A	Catalyst B	Fraction 130-240°C Muchanovo Crude Oil
Gasoline Yield to 110°C% Reference to Hydrogenation Remover	20.2	5.8	9.3 (in ref. to crude oil)
Jet Fuel Yield 130-240°C% in Ref. to Hydrogenation Remover	41.5	33.0	24.1 (in ref. to crude oil)
Density at 20°C	0.784	0.783	0.779
Analyses:			
Boiling Point, °C	133°C	138°C	132°C
5%	140	151	142
50%	171	190	183
95%	221	228	233
End of Boiling, °C	229/98	232/98	244/98

Viscosity/ 20°C	1.23 cst	1.52 cst	1.37 cst
Iodine number	1.1	2.32	1.38
Aromatic substances, weight-%	17.5	4.4	14.9
Olefine, weight-%	0.6	1.6	0.8
Naphthene, weight-%	23.7	47.0	21.7
Paraffins, weight-%	58.2	47.0	62.6
Crystallization point, °C	below-70	-66	-49
Flash point, °C PM.	29	36	26
Sulphur content, weight -%	0.015	0.007	0.12
Ethyl hydrosulphide, weight-%	0.0002	0.0003	0.0026

Table IV

Quality of Diesel Oil, Fraction 240-360°C from the Hydrogenation Remover

	Catalyst A	Catalyst B
Fractional Yield from the Hydrogenation Remover, weight-%	16.7	35.1
Density at 20°C	0.826	0.821
Boiling point	259°C	270°C
5%	265	276
50%	281	297
95%	333	354
End of Boiling	343	360
Cetane rating (Vorberg)	62	68
Aromatic Substances and Olefine, weight-%	12.7%	3.8%
Naphthenes, weight-%	11.1%	15.4%
Paraffins, weight-%	76.2%	80.8%
Viscosity/20°C	6.26 cst	7.53 cst
Solidifying point	-6	-6
Sulphur content, weight-%	0.030	0.012

Table V

Refining Characteristics of the Cracking Catalyst

The experiment was carried out with a catalyst which subjected a heavy crude oil distillate to hydrocracking for 700 hrs. at 470°C and 300 at.; the catalyst was not reactivated before the refining experiment.

Experimental conditions: pressure 300 at., partial pressure of hydrogen 195 at.,
temperature 370°C, gas product ratio 1.2 m^3/L/hr.;
space velocity 0.9 l/l/hr., remover yield 96 weight-%.

Raw material: Mixture distillate of crude oil and tar from low-temperature carbonization (Most).

Density / 20	0.840 Product: density /20	0.808
Boiling point	50°C	45°C
to 200° C	40 Vol. -%	43 Vol.-%
250°C	60 Vol. -%	63 Vol.-%
320°C	89 Vol. -%	91.5%
End of boiling	334/98	349/99
Phenols	4.9 Vol.-%	10 mg/l
Bases (as NH_3)	1046 mg/l	4.6 mg/l
Sulphur content, weight -%	0.72	0.02

In summary it can be said that hydrocracking of heavy crude oil distillates at 300 at. by means of suitable catalysts can be applied, according to requirements, to the production of gasoline or Diesel oil and jet fuel. Cracking of Diesel oil and jet fuel by means of a selectively operating catalyst developed by us consumes less hydrogen and is nowadays very advantageous.

Products obtained from the hydrocracking process, particularly jet fuel, have better chemical properties than similar fractions obtained from primary crude oil.

Application of the hydrocracking process also affords a better utilization of paraffinic, sulphurous crude oils.

The high pressure installation which operates at 300 at. and which was constructed for the production of fuels from low-temperature carbonization tars, can also serve advantageously for hydrorefining of crude oil distillates, for production of lubricants, paraffin and ceresin or be used in their hydrocracking process. One of the advantages of high pressure hydrocracking is that in addition to light and medium fractions, heavy crude oil distillates which boil up to 500°C, can also be subjected to the cracking process without experiencing a quick deactivation of the catalyst. The cracking process can be influenced in such manner, when using a selectively working hydrocracking catalyst, that the main products become Diesel oil and jet fuel.

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Literature

1. Jones, W. A.: Oil Gas J. 53, c. 26; 81 (1954).
2. Acker, A., Choisnet, V.: V. World Petr. Congress section III. Paper 12.
3. Pankov, B. M., Straz, A. G.: CHTTM 6, No. 2, 25-27 (1961).
4. Rozov, S. P., Damilevic, A. T. etc.: CHTTM 6, No. 4 23-27 (1961).
5. Garazimenko, N. M., Jastrebov, G. I. etc: CHTTM 6, No. 4, 27-31 (1961).
6. Grundrod, J.: Sci. Lubrication 10; No. 2, II. 14-16, 18 (1958).
7. Patterson, A. G., Jones, M. C. K.: Oil Gas J. 53, No. 24, X, 92 (1954).
8. Carlsmith, L. E., Haig, R. R.: Petr. Ref. 36, No 9, 233 (1957).
9. Steinberger, I. A.: Chem. Process Eng. 38, 291 (1957).
10. Moreton, A. G.: World Petrol. 27, No. 2, 44 (1956).
11. Demeester, J.: Bull. assoc. techn. du pétrole No. 1 ., 5 (1961).
12. Demeester, J.: Erdöl u. Kohle 14, 464-466 (1961).
13. Schnabel, B., Vecerka, M., Dragoun, J.: Ropa a uhlie 2 (10), 230 (1960).
14. Schnabel, B., Vecerka, M.: Ropa a uhlie 3 (11), 228 (1961).
15. Goldstejn, D. L. Rysakov, M. V. etc.: Chemicky Prumysl 8/33, 574 (1958).
16. Agafonov, A. V.; Rysakov, M. V. etc.: Lecture given at the 3rd International Symposium on Lubricants, GDR (1961).
17. Buttler, R. M., Kartsmark, R.: V. World Petr. Congress Section III. Pater 11.
18. Krönig, W.: Catalytic Pressure Hydrogenation Coals, Tars and Mineral Oils (Springer Publishing House) 1950.
19. Schnabel, B., Večerka, M.: Omnibus Volume of Research Work from the Research Institute for Chemical Exploitation of Lignite, CHE CSSP near Most ČSSR, Part II (in print).

20. Schnabel, B., Vačerka, M.: Freiberg Research Journals (in print).

21. Rappoport, I. B.: Synthetic Fuel Oil II (State Publishing House for Technical Literature in Moscow) 1955.

22. Sherwood, P. W.: Petr. Ref. 28, 97 (1949) and Petr. Ref. No. 11 (1952) S. 93–8.

23. Clough, H.: IEC 49, 673 (1957).

24. Landa, S.: Syntetická paliva SNTL Praha, 1960.

25. Zalai, A., Károlyi, J., Birthler, R.: Chem. Technik 13, 93 (1961).

26. Oil. a. Gas J. 13.4. 1951, S, 122–124.

27. Stormout, D. H.: Oil a. Gas J. 58, Nr. 13, 127 (1960).

28. Scott and Mitarb.: Petr. Ref. 39, 155 (1960).

29. Scott and Mitarb.: Petr. Ref. 39, 101 (1960).

30. Oil a. Gas J. 58, Nr. 16, 104 (1960).

31. Haúsford and Mitarb.: Petr. Ref. 39, 169 u. 199 (1960).

32. Petr. Ref. 39, 199 (1960).

33. McAfee and Mitarb: Petr. Ref. 34, Nr. 5, 156 (1955).

34. Pichler, H., Chervenach, M. and Mitarb.: Petr. Ref. 36, 201 (1957).

35. Pichler, H., Chervenach, M and Mitarb.: Oil a Gas J. Nr. 39 109 (1957).

36. Kazobaschvili, J. R.: Zhurnal Prikl. Khim. 31, 874 (1958).

37. Kazobaschvili, J. R., Golosov, S. A.: CHTTM 5, Nr. 1, S, 8 (1960).

38. Kazobaschvili, J. R.: Trudy inst. nieft. AN SSSR) 13, 195 (1959).

39. Varga u. Mitarb.: Petr. Ref. 36, 196 (1957).

40. Varga u. Mitarb.: Petr. Ref. 39, 182 (1960).

41. Varga u. Mitarb.: CHTTM 5, Nr. 10, S. 11 (1960).

42. Stevenson, Heinemann: ICE 49, 664 (1957).

43. Carlson und Mitarb.: IEC 50 Nr. 7, 1067 (1958).

44. Krafft. O.: Reports from the Research Institute for Chemical Exploitation of Lignite, CHZ ČSSP. Most, ČSSR. Part II (in print).

45. Krafft, O., Mraz, V., Kubicka, R.: Unpublished Results of the Research Institute for Chemical Exploitation of Lignite, CHZ ČSSP.

46. Oil a.Gas J. 59, Nr. 38, 18, 9 (1961) S. 104.