

MANUFACTURE OF DIESEL OIL BY SOLVENT EXTRACTION OF HYDROGENATION MIDDLE OIL

Preliminary tests indicated that of the various solvents tested (methanol, methanol-water, methylformate, methanol-methylformate, furfural, SO₂-propane, SO₂-butane and SO₂-hexane) the combination SO₂-butane was best suited both with respect to yield and the properties of the diesel oil.

Laboratory experiments were carried out with a fraction of the separator product from coal hydrogenation; this fraction had a boiling range of 392 - 617°F.

Above +14°F. no separation into layers takes place, but with decreasing temperature the yield of diesel oil increases until it reaches a maximum at -22°F. Lowering the temperature to -40°F. does not bring any advantages both with respect to yield and quality of the diesel oil. The results of laboratory extractions under various conditions are shown in the attached Table 1. It is assumed that paraffins are practically insoluble in SO₂ at -4°F., but that in the raffinate the concentration of naphthenes and paraffins in SO₂ becomes more and more equal when the temperature is lowered. The best extraction temperature for the manufacture of diesel oil which should contain both naphthenes and paraffins appears to be -40°F.

Extraction with a mixture of SO₂ and butane is a rather flexible process and possible variations in yield and quality of the diesel oil are shown in Table 2.

By increasing the amount of butane or by decreasing the amount of SO₂, the diesel oil yield is increased, whereas the quality of the oil is lowered proportionally.

At a constant ratio of the two solvent components the use of increasing quantities of solvent results in a higher yield and quality of the diesel oil. This indicates that by increasing the amount of solvent the separation of paraffinic and naphthenic hydrocarbons from the other constituents of the oil is improved.

The yield and quality of the diesel oil depends to a large extent on the boiling range of the starting material. A higher yield is obtained when a lower-boiling fraction is extracted.

Since the best extraction results are obtained by carrying out the operation in a column and since the extraction temperature should preferably be -22°F., it is desirable to dewax the oil prior to extraction in order to avoid paraffin separation in the column. Dewaxing is also important with respect to the cloud point of the oil which should be -4°F.

The middle oil was, therefore, dewaxed using SO₂ as dewaxing solvent. Dewaxing of a middle oil of 19.5 API gravity with 70% SO₂ at -4° yielded 19% by weight of wax (40.3 API gravity, 160°F. aniline point and 28.4°F. melting point) and a filtrate (API gravity 15.6) with a cloud point of -26°F.

For the pilot plant tests the following procedure was worked out: The oil-SO₂ mixture from the dewaxing unit is mixed with a definite amount of butane

for the purpose of preliminary refining and for separation into 2 layers; the mixture is cooled to -40°F. and introduced in the middle of the extraction column. The mixture separates in the column into raffinate and extract and these layers are further refined by SO₂ which is introduced at the top of the column and butane which is introduced at the bottom.

This method of operation avoids the necessity of freeing the dewaxed oil from the solvent and the SO₂ used for dewaxing is also utilized as selective solvent.

Dewaxing was carried out in a basket centrifuge with a diameter of 2 feet and a height of 0.8 feet. 26.5 gallons of oil were cooled in an agitator and a definite amount of SO₂ of the same temperature was added. After the mixture had been stirred for 1 hour at this temperature it was centrifuged in a precooled centrifuge. The speed of filtration was 29.4 gallons per square foot per hour at a speed of 2,000 r. p. m. After the filtration the wax was dried by centrifuging at 2,800 r. p. m. for 5 minutes. To obtain a pure wax the product was washed with a suitable amount of SO₂ at 500 r. p. m.

With a middle oil of API gravity 19.2 and aniline point of 60°F., the following results were obtained on dewaxing at different temperatures:

Temperature °F.	Oil Charge gals.	SO ₂ for dewaxing gals.	SO ₂ for washing gals.	Wax Yield lbs.
-2.2	26.4	15.8	7.9	15.5
-0.4	26.4	15.8	7.9	12.9
+1.4	26.4	15.8	7.9	11.0

The wax yield can be increased by increasing the amount of SO₂ as indicated in the following table:

Temperature °F.	Oil Charge gals.	SO ₂ for dewaxing gals.	SO ₂ for washing gals.	Wax Yield lbs.
-7.6	26.4	9.2	3.9	11.6
-2.2	26.4	15.8	7.9	15.5

Filterability was found to be good in all experiments. The dewaxing run carried out with 9.2 gallons of SO₂ is of special importance since it was found in refining experiments that this SO₂ concentration is especially favorable for preliminary refining. It was, however, soon found that with this quantity of SO₂ the dewaxing temperature of -4 is not sufficient to remove the paraffin completely enough to avoid wax separation in the column. Therefore, the oil to be used in the subsequent refining steps had to be dewaxed at -22°F. At temperatures below -22 and using 9.2 gallons of SO₂, the speed of filtration decreased to half of its previous value so that this temperature region is without practical importance. When more than 50% SO₂ is used, stratification occurs already in the course of the dewaxing operation.

The wax obtained by centrifuging is of better quality and is obtained with higher yields than the wax prepared in the laboratory.

The experiments were carried out in a column of 2.8 inch diameter packed with Raschig rings. Butane was introduced in the lower part of the column, whereas SO₂ was injected at the top; the mixture of oil and SO₂ from the pre-

liminary refining operation was introduced in the center of the column. The charge rate was 0.25 - 1.5 gallons per hour. The use of gear pumps for charging oil and solvent was unsuccessful due to vapor lock and because the lubricating oil of the pumps was dissolved after a very short time and the viscosity of butane is too low to take its place. Consequently, butane was passed into the column by means of its own vapor pressure and the oil-SO₂ mixture was introduced under nitrogen pressure. The use of a syphon for controlling the withdrawal of extract was found impossible and the syphon was, consequently, replaced by a valve.

2 coal hydrogenation middle oils were used in these experiments. They had the following physical data: Oil 1, API gravity 16.1, aniline point 55°F., cloud point 23°F., pour point 0.4°F. and boiling range 446 - 635°F., whereas the oil 2 had API gravity 17.2, aniline point 57°F., cloud point 23°F., pour point 14°F. and boiling range 365 - 617°F.

The course of the refining operation was as follows:

After dewaxing at -22°F. the filtrate (about 80 gallons) was pumped into a pressure surge tank where the desired SO₂ concentration could be adjusted. From here the oil-SO₂ mixture was passed by nitrogen pressure into a low-temperature cooler where it was mixed with the desired amount of butane and cooled to -40°F. This part of the process is called "preliminary refining" since raffinate and extract are formed at this stage but cannot separate while flowing through the low-temperature cooler. The mixture is introduced in the center of the extraction column where it separates into raffinate and extract and is further refined by butane and SO₂ which are introduced in the column at the bottom and the top, respectively. Raffinate and extract flow into the evaporator, are freed from solvent and drawn off hourly. 30 different experiments were carried out.

The following variables of the refining process were investigated: The quantity of butane used in the preliminary and final (column) treating, the butane ratio in preliminary and column treating, the SO₂ volume used in the column and the SO₂ ratio in preliminary and column treating. The following observations were made:

With diesel oil yields up to 40% by volume, the separation between raffinate and extract could be easily seen. The experiments, consequently, proceeded smoothly and only small differences in density and aniline point were observed in the products withdrawn hourly. It did not make any difference whether the mixture coming from the preliminary refining step was introduced into the raffinate or extract layer in the column. At higher yields no stratification could be observed in the sight glass of the column which resulted in carry-over of extract in the outgoing raffinate. This resulted in larger fluctuations in the properties of the samples.

The relation of the quantity of butane and the degree of refining is given in Tables 4 and 5. The quality of the raffinate is lowered proportional to the increase in yield. It is advantageous to use a larger percentage of butane in the column because experiments with the same total amount of butane, but with variations in the ratio of butane used in preliminary to butane used in column refining, indicate that higher yields can be obtained by using a higher percentage of butane in the column.

When the amount of SO₂ was increased, the yield of raffinate decreased but its quality was improved. With the same total amount of SO₂ better effects were obtained when the amount of SO₂ used in the column was larger than that used

in the preliminary refining step. The best results were obtained, consequently, when the entire SO_2 was added in the column. This has the following disadvantages:

1. The SO_2 used for dewaxing must be completely removed prior to treating in the column.
2. At a raffinate yield exceeding 45% by volume no separation between raffinate and extract can be seen, which makes it difficult to control the process.

By using SO_2 in the preliminary treatment, these difficulties can be avoided and the separating zone becomes more distinct when the SO_2 used in the preliminary treat is greater. Yields up to 56% by volume can be obtained by using 35 - 40% SO_2 in the preliminary refining step without causing the separating line to disappear. According to the experimental results, the best operating practice consists in using 35% by volume of SO_2 for dewaxing and using the entire quantity of SO_2 in the filtrate for preliminary refining.

The quantities of solvent to be used in the refining process are limited. When 37% SO_2 is used for preliminary treating the least possible total amount of SO_2 is 75%. When less SO_2 is used, no separation in the column takes place. This minimum quantity of SO_2 , however, determines the butane volume to be used. Therefore, the amount of butane required for optimum results is 200 - 250%. The butane concentration has not only a lower but also an upper limit. If, at an average throughput of 1 gallon of oil per hour, more than 175% by volume of butane is used for treating in the column, no clear separation between raffinate and extract can be obtained.

On the basis of these findings, it was possible to obtain diesel oils with the following yields:

An oil of a cetene number of 52 - 55 could be obtained with a yield of 36 - 38% by weight (based on the feed), an oil with a cetene number of 48 was obtained with a yield of 41% and an oil with a cetene number of 40 - 42 was obtained with a yield of 46 - 49%. The oils had a light color after contacting with 2% clay, they had a good odor and a cloud point below -4°F . By the addition of a pour-point depressant (Paraflow), a minimum of 50% of the distillate obtained from the paraffin wax previously separated could be incorporated in the finished oils without exceeding a cloud test of -4°F . For 50% of paraffinic distillate it was sufficient to add 0.1% Paraflow. The diesel oil yield was thereby increased by 3% without change in the cetene number. By the addition of the entire amount of paraffin wax separated, the yield was increased by about 10% but the cloud test of this oil with a cetene number of 50 was only $+6.8^\circ\text{F}$.

A charge stock which is richer in paraffin than the oils used in these experiments would, obviously, give higher yields.

The results of the column extractions were considerably better than those obtained in single extraction experiments in the laboratory. The yield was about 15% higher for oils of equal density and aniline point. The solvent requirements for SO_2 are smaller but for butane greater as compared to laboratory experiments. The SO_2 requirements are 75 - 110% by volume, including the SO_2 required for dewaxing, and 200 - 250% by volume for butane (percentages based on dewaxed oil).

The properties of the product obtained by the solvent refining process are indicated in the following table:

	<u>Expt. 20</u>	<u>Expt. 26</u>
Hard asphalt %	0	0
Pour point °F.	-20	-26
Temperature limit } for filterability } °F.	-0.4	-0.4
Flash point, open cup, °F.	190	194
Flash point P.M. °F.	178	185
Ash %	Trace	Trace
SUS/68°F.	39	39
n_D^{20}	1.4842	1.5088
Heat of combustion, Btu/lb.	19,310	19,000
Heating value, Btu/lb.	18,100	17,890
Mol. wt.	182	197
Cetene No.	52	39.5
Conradson Carbon Residue %	0.06	0.06
Aromatics %	41	62
Olefins %	9	12
C %	87.32	88.04
H %	12.35	11.32
N %	0.18	0.20
S %	0.066	0.16

Engine tests carried out in a Junkers 2-cylinder - 2-stroke engine showed that the 2 diesel oils whose properties were given in the preceding table gave a higher output for the same number of revolutions because of the difference in heating value per liter as compared to the reference fuels. At the same engine output the solvent treated oils showed a somewhat higher fuel consumption. The ignition delay of the two fuels was greater than that of the regular diesel fuels used for reference purposes; the raffinate from experiment 18 was found to be unsuited for the Junkers motor which is very sensitive with respect to the ignition properties of the fuel.

The smoke formation of the raffinates was as small as that of the other fuels and the formation of residues could not be observed in the short operating period.

The starting behavior of the fuels at 50--60°F. was unsatisfactory.

For the calculation of the economics of the process, the following six processes were compared:

1. Diesel oil from separator product from coal hydrogenation prepared by subsequent hydrogenation with catalyst 5058.
2. Diesel oil from the separator product from tar hydrogenation prepared by subsequent hydrogenation with catalyst 5058.
3. Diesel oil from the separator product from coal hydrogenation prepared by extraction with SO₂-butane.
4. Diesel oil from the separator product from tar hydrogenation prepared by extraction with SO₂-butane.
5. Diesel oil obtained by the low-temperature, high-pressure hydrogenation of brown coal tar at higher temperature than regularly used.
6. Diesel oil obtained by the low-temperature, high-pressure hydrogenation of brown coal tar at the regular temperature.

For the manufacture of diesel oil by extraction a raffinate yield of 50% was assumed, together with a solvent requirement for SO₂ and butane equal to 1.5 x the volume of the middle oil to be extracted. Since interest was centered in the maximum yield of diesel oil, cases 1 - 4 were calculated not for equally high diesel oil production but for the maximum possible yield of diesel oil. Therefore, for cases 3 and 4 an additional production of diesel oil from the SO₂ extract by hydrogenation using catalyst 5058 was assumed.

Obviously, at a lower production of diesel oil, its manufacturing cost could be lowered due to the credit obtained from the correspondingly higher yield of gasoline.

The following tabulation shows the product distribution assumed in the economic calculations:

Case	1	2	3	4	5	6
Yield of						
Wax %	-	-	4	3	5	20
Gasoline %	49	49	30	28	33	24
Lube Oil %	-	-	-	-	-	14
Diesel Oil %	51	51	66	69	62	42

When the gasoline obtained in all processes is credited uniformly with the actual selling price, the lowest manufacturing costs are obtained for diesel oil prepared according to case 2.

If the price so obtained is taken as equal to 1, the comparative prices for the other processes are as follows: case 1 - 1.23, case 3 - 1.3, case 4 - 1.1, case 5 - 1.05 and case 6 - 1.04. If, however, that price for gasoline is used which is calculated from the manufacturing cost in case that the hydrogenation middle oils are completely converted to gasoline, the prices for diesel oils obtained by extraction or by refining through hydrogenation become almost equal.

Considering the fact that the solvent extraction of middle oils has not been tried out on a large scale, especially with respect to corrosion in the case of the extraction with SO_2 of oils containing phenols, there exists no incentive on the basis of the experimental results to introduce the solvent refining process into the plant.

Table 1

Effect of temperature on extraction.

Coal middle oil (boiling range 374 - 617°F, API gravity 18.6, aniline point 52°F.)
extracted once with 125% butane and 175% SO₂.

<u>Extraction Temperature</u> °F	Yield % by wt.	<u>Raffinate</u>	
		API gravity	Aniline Point°F.
-4	33.1	32.1	124
-22	37.3	33.2	128
-40	38.5	33.8	128
-58	38.7	34.2	128

Coal middle oil (boiling range 374 - 617°F., API gravity 19.7, aniline point 54°F.)
original sample extracted once with 70% butane and 120% SO₂; extract treated with
40% butane; combined raffinates extracted with 20% SO₂.

<u>Extraction Temperature</u> °F	Yield % by wt.	<u>Raffinate</u>		<u>Extract</u>
		API gravity	Aniline Point °F	API gravity
-13	27	44.1	169	10.6
-22	33	41.7	159	9.7
-31	34	39.4	154	8.6
-40	38	37.3	143	8.4

Table 2

Effect of Quantity of Solvent on Extraction

Effect of quantity of butane

Butane % by vol. of oil	SO ₂ % by vol. of oil	Extraction Temp. °F	Raffinate Yield % by wt.	API Gravity	Aniline Pt. °F
-	-	-	Feed	18.7	52
100	100	-40	38.8	32.3	117
160	100	-40	43.9	31.7	112
200	100	-40	47.4	30.2	104

Effect of quantity of SO₂

-	-	-	Feed	19.2	66
125	128	-40	46.4	33.2	126
125	160	-40	43.7	34.2	129
125	175	-40	42.8	34.8	132

Effect of total quantity of solvent at constant butane-SO₂ ratio

-	-	-	Feed	18.1	66
124.5	127.3	-40	46.4	33.3	126
96.6	100	-40	44.3	32.8	125
127.3	127.3	-49	37.3	34.4	130
75	75	-49	37.4	31.2	123

Table 3

Extraction in several stages

Butane % by vol. of oil	SO ₂ % by vol. of oil	Extraction Temp. °F	Raffinate		
			Yield % by wt.	API Gravity	Aniline Point °F
			Feed	18.7	52
100	100	-40	38.8	32.3	117
1 x 40 + 2 x 30	1 x 40 + 2 x 30	-40	36.8	33.6	123
1 x 40 + 3 x 20	1 x 40 + 3 x 20	-40	34.1	35.7	134

Table 4

Effect of butane used for preliminary refining on over-all refining
(coal middle oil 2)

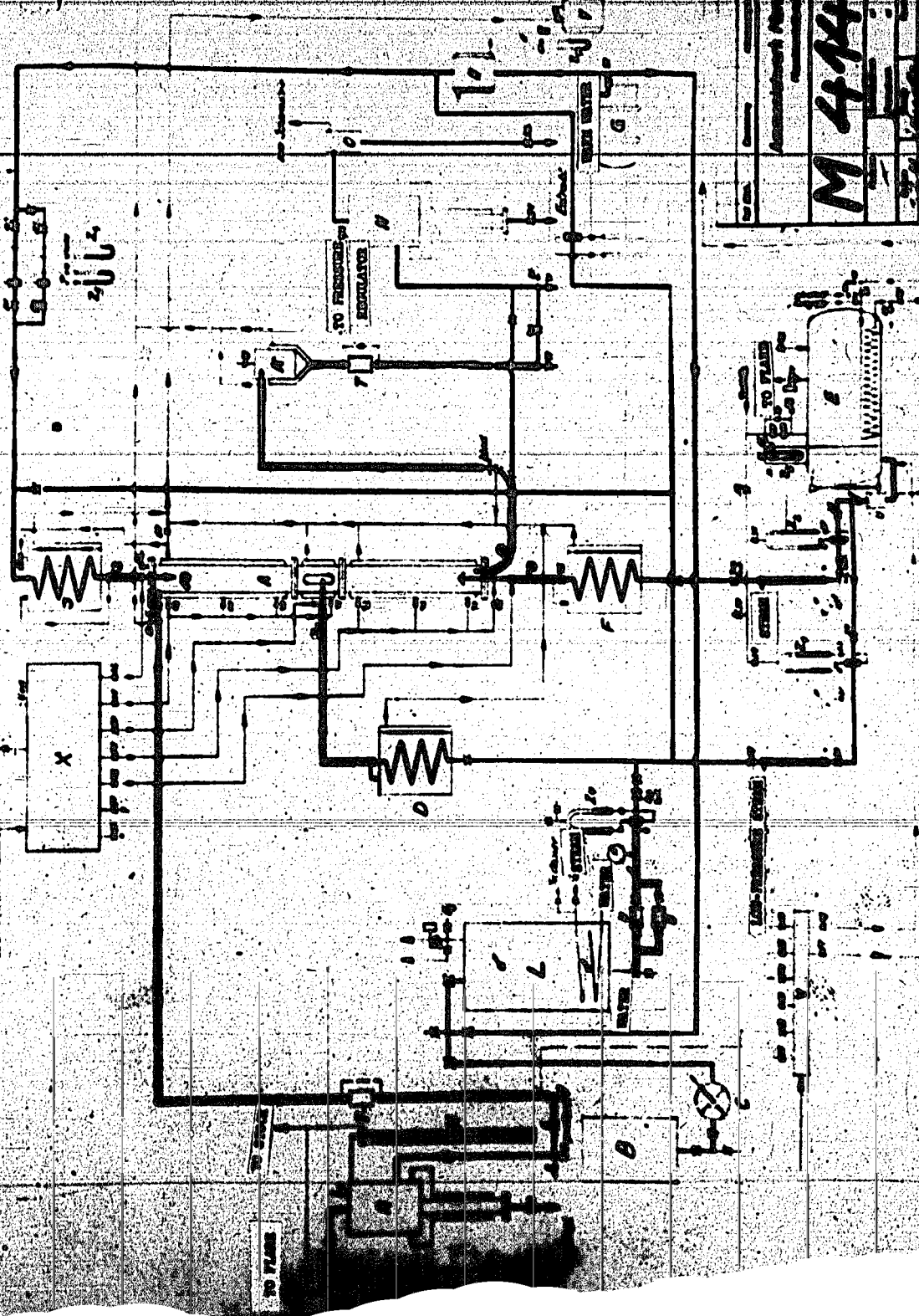
Expt. No.	Butane		SO ₂		Raffinate		Aniline Point °F	Cloud Point °F	Pour Point °F	Cetene No.	Extract API Gravity
	Pretrat % of oil	Column % of oil	Pretrat % of oil	Column % of oil	Yield % by wt.	API Gravity					
25	24.6	146.7	38.7	41.6	46	28.7	93	-9	-18		4.2
18	73.2	146.4	38.2	41.5	61.6	25.2	71	-20	-29	42	3.4
26	102.2	151.8	38.7	43.6	66.1	25.7	71	-11	-26		3.6

Table 5

Effect of butane used in column on over-all refining
(coal middle oil 2)

30	73	121.3	35.4	41.3	49.5	26.4	78	-9	-27		3.6
18	73.2	146.4	38.2	41.5	61.6	25.2	71	-20	-29	42	3.4
28	73.4	171.3	37.5	41.5	64.7	25.0	71	-11	-26		3.6

- A. GASES
- B. OIL-DRY VALVE
- C. OIL-DRY PUMP
- D. AIR-DRYING CYCLES FOR EXTRACTOR
- E. EXTRACTOR PRESSURE VALVE
- F. EXTRACTOR CYCLES
- G. AIR PRESSURE VALVE
- H. AIR EXHAUSTORY
- I. AIR COOLER
- J. EXTRACTOR CYCLES
- K. OIL-DRY PRESSURE VALVE
- L. EXTRACTOR REGULATORY
- M. EXTRACTOR REGULATORY
- N. EXTRACTOR
- O. EXTRACTOR EXHAUSTORY
- P. EXTRACTOR
- Q. EXTRACTOR
- R. EXTRACTOR
- S. EXTRACTOR
- T. EXTRACTOR
- U. EXTRACTOR
- V. EXTRACTOR
- W. EXTRACTOR
- X. EXTRACTOR
- Y. EXTRACTOR
- Z. EXTRACTOR



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