RESTRICTED

ENCLOSURE (B)

ENCLOSURE (B) 1

STUDIES ON THE PRODUCTION OF DIESEL FUEL BY LIQUID SO_2 EXTRACTION

by

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

This investigation was begun in order to obtain a high cetane rating diesel fuel with low pour-point from petroleum kerosenes by the Edeleanu Process. The most significant results were that the aromatic hydrocarbons were for the most part removed from the kerosenes and the raffinate gave about 60-70 cetane rating.

I. INTRODUCTION

It was well known that the aromatic hydrocarbon components decreased the cetane value of petroleum oil. Accordingly, in order to obtain high cetane diesel fuel oil from petroleum, it was necessary to remove the aromatic hydrocarbon from the crude oil. In our laboratory, various kinds of petroleum oils were extracted under various conditions. This work was carried out by Naval Eng. Lieut. S. SONODA, C. NISHIMURA Naval Eng. Y. FUJIEDA and others, during the period Apr., 1942-Sept., 1944.

II. DETAILED DESCRIPTION

A. Test Procedures

Liquid SO_2 was inserted into a 3 liter flask which was maintained at the required temperature by dry ice. The mixture of one liter sample and liquid SO_2 in various ratios was mixed with a stirrer for 30 minutes, then, the raffinate and extract respectively were allowed to flow into the SO_2 evaporator, where SO_2 was evaporated by heating up to 80°C electrically. The diagram of extraction apparatus is given in Figure 1(B)1.

The properties of the products were determined by the ordinary methods. The method of measuring the spontaneous ignition temperature was mainly that of J. S. Lewis (Japanese Chem. Soc., 1558, (1927)), as shown in Figure 2(B)2. The sample oil (0.1cc) was first introduced into a reaction vessel (240cc pyrex glass tube), and the vessel was evacuated. The vessel was heated at the rate of 4°C/min., after which CO_2 free air was introduced into it. The increase in vapour pressure in the vessel was recorded every minute. The spontaneous ignition temperature was measured, at the time when a sudden ebullition of gas occurred in the mercury manometer, caused by the ignition and burning of the sample in the vessel.

B. Experimental Results

1. Petroleum sample from various sources were extracted with 100 wt % of liquid SO_2 at temperature -10°C. The results are given in Table I(B)1. According to this table, it was concluded that paraffinic petroleum kerosenes were more suitable than aromatic ones, for providing diesel fuel of high cetane rating.

2. Tarakan kerosene (aromatic) and Sanga Sanga kerosene (paraffinic), both obtained from Borneo, were extracted with 100% of liquid SO_2 at temperature -20°C. These results were given in Table II(B)1, Figure 3(B)1, Table III(B)2 and Figure 4(B)1. The appreciable tendencies in those results were as follows:

   a. The extraction effect for Tarakan kerosene was not appreciable.

   b. The effect for Sanga Sanga kerosene was recognized to be appreciable.

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c. The extraction effect increased with higher boiling point in the same kerosene.

3. A pilot plant which was begun on 15 August 1945, had a capacity of 100 liters per hour; the flow sheet was exactly the same as the so-called Edeleanu Process.

The pre-cooled kerosene raw stock was fed into the bottom of the extractor, and the pre-cooled liquid SO_2 descended from the top in a spray, and the solvent and oil were mixed with each other in counter current, the solvent extracting the aromatic hydrocarbons from the oil. The optimum conditions for operating the extraction tower were :

Extraction temperature ..... -25°C
Extraction pressure ..... atmospheric
Solvent ratio 100%

The remaining SO_2 in the raffinate and extract oils was removed by heating the SO_2 extractors up to temperature 80°C. However, many difficulties in operation were experienced, due to the leakage of SO_2 from valve glands and packings of plunger pumps employed. The properties of raw stock and raffinate produced from the preliminary operation are given in Table IV(B)1. Roughly, the yield of raffinate was thought to be about 70%.

III. CONCLUSION

In the research laboratory experiments, it was recognized that it was possible to remove the great part of the aromatic hydrocarbons from petroleum.

The extration effects increased almost proportionally with the increase of boiling range and paraffinicity of the raw kerosenes.

In the pilot plant operations, many difficulties were experienced, chiefly due to the leakage of SO_2 gas from valve glands. It was found to be very difficult to operate the Edeleanu Plant with packing materials produced in Japan.

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Table I(B)1
PROPERTIES OF RAFFINATE*

Sample	Yield (%)	Sp.gr (15/4°C)	Viscosity (R-1.30°C)	Flash pt (°C)	Pour pt (°C)	Cetane Value
Bahrein (204-365°C)	86.2	0.8093	33.0	none	-24	64.0
Oha (259-372°C)	82.4	0.8834	52.1	none	-29	45.4
Kettleman Hills (50% topped residue)	85.0	0.8194	31.8	none	-40	54.5
Midway (200-350°C)	72.5	0.8534	38.0	none	-26	49.5
Tarakan (200-300°C)		0.8606	34.6	none	-30	49.0
Innai, Japan (200-300°C)	86.0	0.8582	34.8	none	-50	39.3
California (200-300°C)	77.5	0.8474		none	-45	48.3
Tarakan (F.D.-60%)	72.4	0.8965	44.6	none	-33	41.7
California (217-385°C)	71.9	0.8603		none		48.2
Mexico (200-350°C)		0.8191	36.4	none	-12	65.7
Sumatra (164-255°C)	88.4	0.7951	30.0	none	-44	51.2
Tarakan (105-356°C)	67.5	0.8571		none	-1	45.4

*Extraction Temp - 10°C
Solvent ratio 100%

Table II(B)1

EXTRACTION EFFECTS FOR TARAKAN KEROSENE

	Tarakan Kerosene (200~300°C)	Fraction (°C) 200~220 A	200~220 B	220~240 A	220~240 B	240~260 A	240~260 B	260~280 A	260~280 B	280~300 A	280~300 B	300~320 A	300~320 B	320~340 A	320~340 B	340~D.P A	340~D.P B
Sp.gr. (15/4 °C)	0.8960	0.8512		0.8666	0.8699	0.8811	0.8750	0.8942	0.8890	0.9030	0.8963	0.9166	0.9065	0.9329	0.9170	0.9458	0.9385
Viscosity (S-1 30°C sec)	41.4	30.6		32.8	32.8	34.8	35.0	38.4	38.2	46.0	44.4	53.0	54.6	70.8	72.8	130.8	167.2
Flash pt. (°C)	62.0	38.5		52.8	58.0	60.5	80.0	86.5	98.0	99.5	115.0	122.5	126.0	131.5	114.5	140.0	96.5
Pour pt. (°C)	18.0	below -30		below -30	below -30	below -30	below -40	below -30	below -30	-44	-37	-21	-26.5	-16	-13	-3.8	+6.0
Cetane Value	34.0	32.0		32.9	33.4	34.0	33.1	33.5	34.9	34.6	37.1	31.1	36.9	35.7	36.3	37.7	
Aniline pt. (°C)	74.2	58.9		62.8	54.9	64.2	56.1	70.4	57.6	75.8	58.5	82.8	58.9	88.3	57.8	87.3	57.7
Diesel Index					47.4		49.3		51.2		52.4		53.2		52.9		51.9
Surface Tension (dyn/cm 25°C)					26.0		26.4		26.6		27.7		28.0		29.8		
Spont. Ignit. Temp. (°C)						24.0											
Unsaturates and Aromatics	48.2	16.0		22.2		24.0		30.8		38.5		50.7		61.5		73.6	
Naphthenes and Paraffines	52.0	84.0		77.8		76.0		69.2		61.5		49.3		38.5		26.4	

B: Raffinate

Table III(B)1

EXTRACTION EFFECTS FOR SANGA SANGA KEROSENE

	Sanga Sanga Crude Petroleum	Fraction (°C) I.B~180 A	I.B~180 B	180~200 A	180~200 B	200~220 A	200~220 B	220~240 A	220~240 B	240~260 A	240~260 B	260~280 A	260~280 B	280~300 A	280~300 B	300~320 A	300~320 B
Sp.gr. (15/4°C)	0.867		0.7766		0.7826		0.7918	0.8487	0.8019	0.8670	0.8128	0.8764	0.8214	0.8818	0.8272	0.8850	
Viscosity (S-1 30°C sec)	36.4		27.1		27.7	29.2	28.7	30.6	30.3	33.4	31.8	35.2	33.9	40.6	37.7	45.7	
Flash pt. (°C)	27.0		6.1		14.5	58.2	49.0	68.5	69.0	92.0	85.0	106.5	97.5	114.5	114.5	70.5	
Pour pt. (°C)	20.0		below -30		below -30	below -30	below -30	-33.0	-41.5	-20	-34.5	-9.5	-22.5	5.5	-3.0	18.5	
Cetane Value	48.9				43.7	43.1	48.3	43.7	52.6	44.3	55.1	44.9	61.4	46.9	65.4	48.5	
Aniline pt. (°C)	Impossible to measure		54.1		58.7	76.2	64.6	77.3	69.8	82.0	73.6	85.9	77.6	90.6	84.0	95.8	
Diesel Index	Impossible to measure																
Surface Tension (dyn/cm 25°C)	Impossible to measure																
Spont. Ignit. Temp. (°C)	Impossible to measure		250		255		228		227		230		227		235		
Unsaturates and Aromatics	Impossible to measure					55.0		51.3		59.2		61.0		60.4			
Naphthenes and Paraffines	Impossible to measure					45.0		48.7		40.8							

A: Raw Kerosene

B: Raffinate

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Table IV(B)1
PROPERTIES OF RAW MATERIALS AND PRODUCTS

	Kerosene (Sanga Sanga 200-260°C)	Product (Raffinate)
Yield (%)		70
Sp. gr. (15/4°C)	0.8487	0.8129
Viscosity (R-1 30°C sec)	30.6	29.9
Flash pt. (°C)	58.5	69.0
Pour pt. (°C)	-33.0	-39.5
Conradson's carbon (%)	Trace	Trace
Ash (%)	Trace	Trace
Impurities (%)	Trace	Trace
Cetane Value	43.1	65.0
Aniline pt.	67.3	75.5
Sp. Ignit. Temp.(°C)	293	225
Unsat. and arom. (%)	55.0	13.0
Naphthene and Paraffin (%)	45.0	87.0

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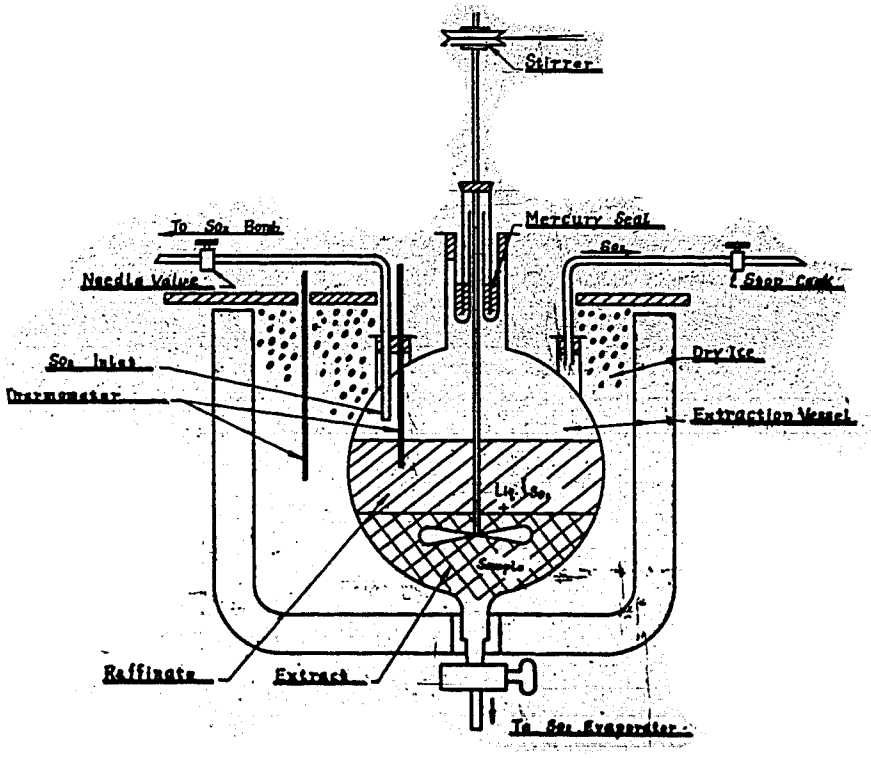

Figure 1(B)1
DIAGRAM OF EXTRACTION APPARATUS

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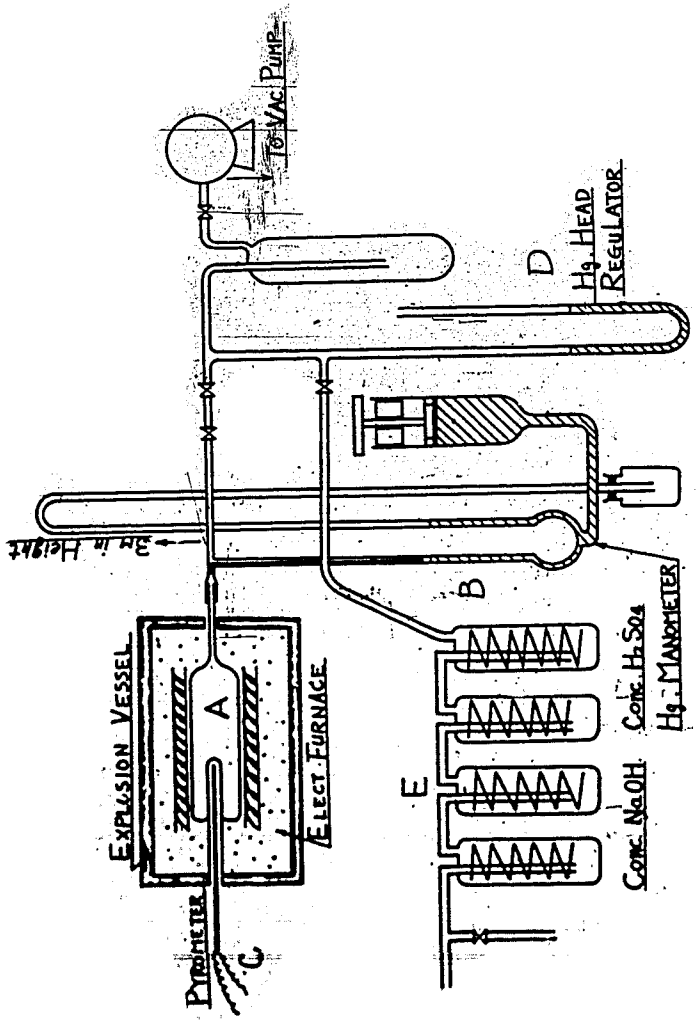

Figure 2(B)1.
APPARATUS FOR MEASURING SPONTANEOUS IGNITION TEMPERATURE

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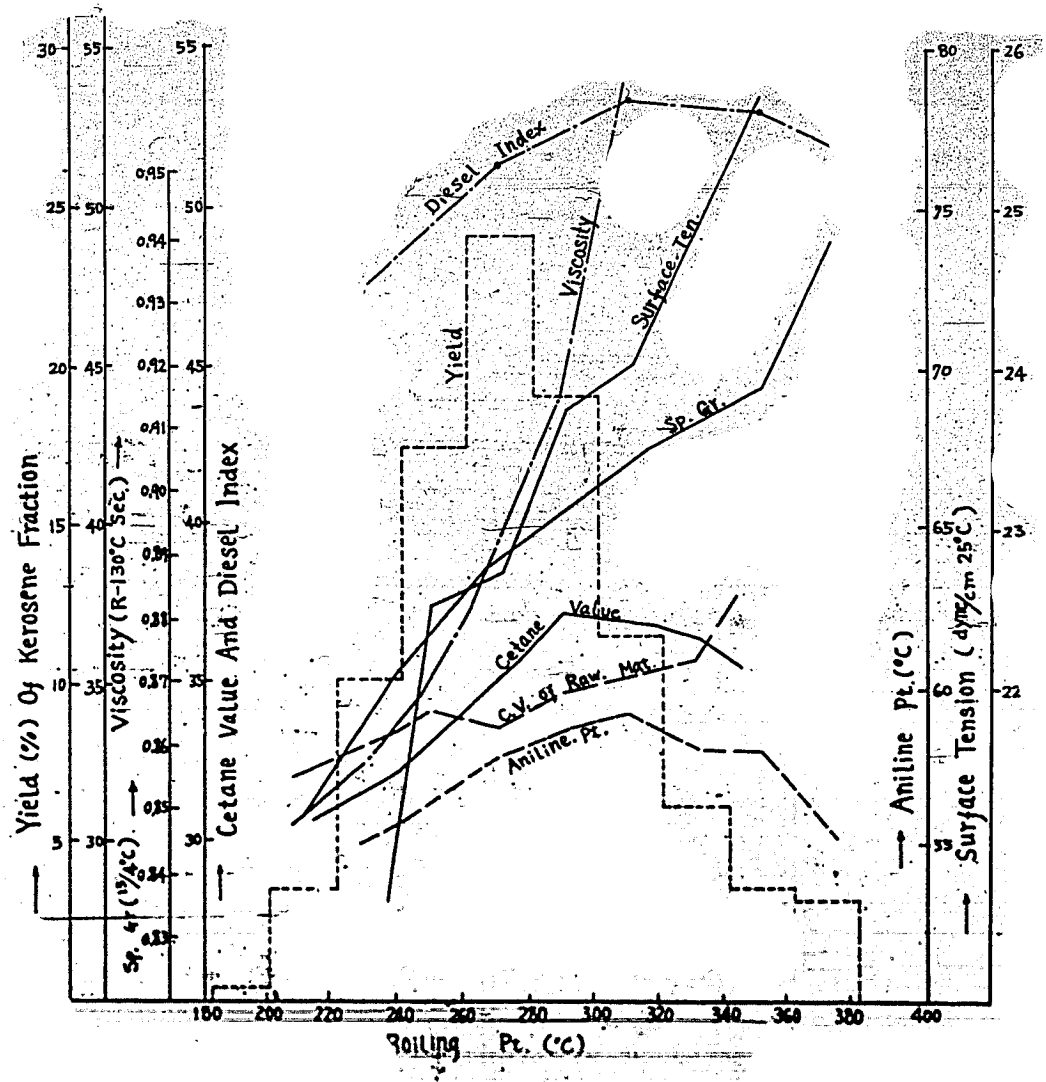

Figure 3(B)1

RELATIONS BETWEEN B.P. OF TARAKAN KEROSENE RAFFINATE AND ITS DIESEL PROPERTIES

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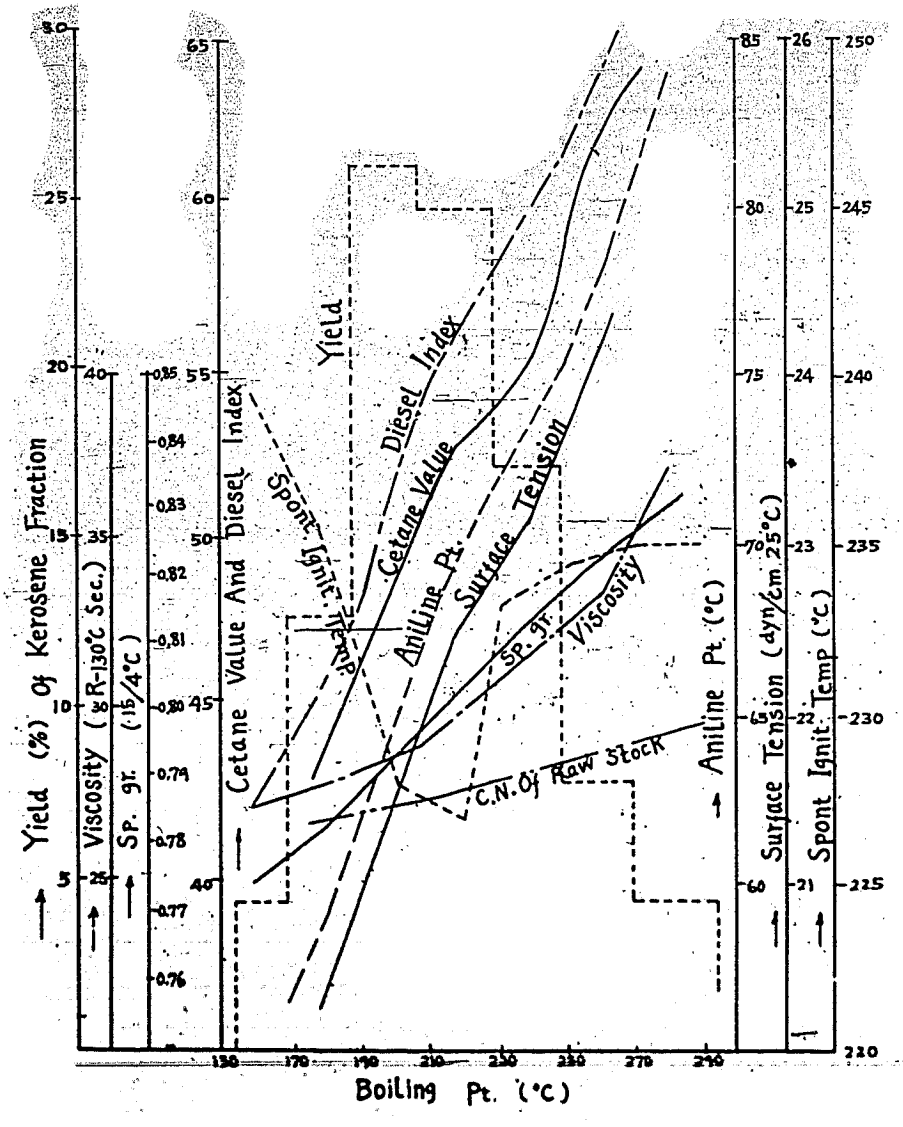

Figure 4(B)1

RELATIONS BETWEEN B.P. OF SANGA SANGA KEROSENE RAFFINATE AND ITS DIESEL PROPERTIES