

T-1004

VISCOSITY BREAKING OF AROMATIC EXTRACTS
FROM LUBRICATING-OIL PROCESSES

By

Alvaro Murcia A.

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Refining Engineering.

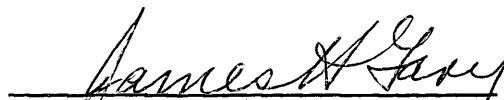
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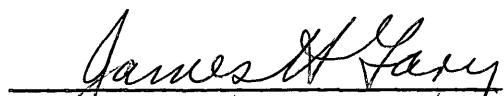

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ABSTRACT

Finding profitable applications for by-products has always been a problem in the refining of petroleum; a possible application for aromatic extracts from lubricating-oil processes would be as aromatic solvents, but their high viscosity (60 to 120 cs at 100°F) and their very low volatility (average bp 750°F) are the main obstacles for this solution to be practicable.

The thermal stability of aromatic rings gives thermodynamic support for the transformation of these extracts using a mild thermal decomposition process; viscosity breaking applied at 700°F, 40 psi and 1060 sec of contact time proves to be effective giving 25% conversion by weight into a light aromatic product characterized by a very low viscosity (1 cs at 100°F) and relatively high volatility (average bp 300°F); the heavy portion of the visbroken products is characterized by a moderately low viscosity (30 cs at 100°F) and a low volatility (average bp 680°F).

Problems in this operation were the coke deposition and gas production (8% by weight); decomposition at a higher level of temperature and pressure adversely changed the quality of the products.

Because this particular field has not been previously investigated, this investigation opens the doors to the production of aromatic solvents using a procedure already familiar to the petroleum refining industry.

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INTRODUCTION

There is a large demand for aromatic solvents in the wood preservation industry to dissolve the organic pesticides and preservatives used in this field. Highly aromatic solvents are very expensive, and inexpensive solvents such as kerosine dissolve only relatively small amounts of the organic materials.

From one of the intermediate steps of lubricating-oil fabrication, solvent extraction, a highly aromatic material is obtained as an extract for which there is no present market; in order to get rid of it, it is common practice to blend it with the feed to the catalytic cracking units. But this extract is a poor feed stock for catalytic cracking because of its low gasoline and high carbon yields and, as extracted, this aromatic material has too high a viscosity and too low a volatility to be used as pesticide solvent.

It is a well-known fact that the molecular weight and complexity of the structure of the hydrocarbons of petroleum increase with the increasing boiling range, but the investigations dealing with the individual components of the heavier petroleum fractions have proven practically hopeless owing to the enormous number of constituents present in those fractions. What is always hoped for is the determination and identification of the chemical constituent classes by means of ring analysis. Heavy distillates of almost all kinds of crude oils have been found to consist predominantly of aromatics and naphthenes in highly condensed forms.

The ambiguity of these identifications and the complexity of the hydrocarbon mixtures give support enough to assume the presence in these mixtures of components which can be classified as mixed aromatic-aliphatic hydrocarbons. It is also a well-known fact that the heat of formation of aromatic structures is always greater than that calculated from normal bond energies of aliphatic double and single bonds; consequently there is thermodynamic support to the possibility of transforming the aromatic-aliphatic hydrocarbons by means of a mild thermal decomposition.

Applying the previous reasoning to the aromatic extract from lubricating-oil processes and assuming that the high viscosity of this material is caused by the complexity of the structure of the aromatic-aliphatic hydrocarbons, again there is thermodynamic support to the idea of transforming this material into another aromatic mixture from which it could be possible to obtain, by fractionation, at least one aromatic fraction characterized by a higher volatility and a lower viscosity than the parent compound.

The main objectives of this investigation are to determine the feasibility of applying a mild decomposition process to an aromatic extract from lubricating-oil processes and to open the doors to additional research in this direction looking for production of aromatic solvents at lower costs of fabrication. From the existing thermal decomposition processes, viscosity breaking was chosen because it is the only one characterized by mild conditions of decomposition. The application of viscosity breaking to this particular stock along with the search for optimum conditions constitute the development work of this thesis.

The literature survey conducted by the author produced no evidence of the application of any mild thermal decomposition to aromatic fractions of petroleum distillates;

consequently the theoretical background of this thesis had to be the large amount of information existing on thermal cracking and pyrolytic decomposition of petroleum hydrocarbons.

The viscosity breaking process proved to be effective for attaining transformation of the aromatic extract (15.6°API, 119 cs) into a product which was separated into a light fraction (37.5°API, 1.25 cs) and into a heavy fraction (11.6°API, 29.5 cs). The operation was carried out on a bench-scale furnace by pumping the aromatic stock once through a 1/4 in diameter pipe coil at temperatures ranging from 700 to 800°F and pressures ranging between 25 and 125 psi; the reactor was operated for 45 min using a residence time of 1060 sec; the rate of coke deposition was very high in contradiction to the statement that viscosity breaking is a non-coking process.

The results obtained prove that by use of a mild thermal decomposition it is possible to reduce the viscosity of highly aromatic extracts. The results also prove that mixed aromatic-aliphatic hydrocarbons are present in these aromatic materials and that the high viscosity of the original extracts can be attributed, at least in part, to the lateral chains of the aromatic-aliphatic hydrocarbons.

As far as the practical aspect of this study is concerned, the economics and design factors still have to be considered: that is, the optimum temperature, pressure, and residence time must be determined by additional experiments, together with a complete study of the solvency properties and characteristics of the products obtained.

DEFINITIONS

To clarify the field in which this investigation is developed and the meaning and extension of the thermal-process objective of this thesis, the author presents definitions of the two most important thermal-processes related to the work.

Cracking

Cracking is the term commonly used for the thermal and catalytic decomposition of hydrocarbons, particularly as practiced in the refining of petroleum where the operation is mainly used for the production of motor fuel. The purpose of cracking is primarily to produce low-boiling constituents by breaking down the largermolecules (Frolich and Fulton, 1938, p. 2099).

Viscosity breaking

Viscosity breaking or viscosity lowering is a mild, liquid-phase thermal decomposition process used to convert

heavy- and high-viscosity petroleum stocks into lower viscosity fractions suitable for commercial use.

The differences between cracking and viscosity breaking are:

- 1) cracking may be thermal or catalytic; viscosity breaking is basically a thermal process, although catalytic viscosity breaking has been performed on a laboratory scale, but never on commercial installations (Sachanen, 1948, p. 371).
- 2) The cracking operation may be performed either in the liquid- or gas-phase or both combined; viscosity breaking is performed in the liquid-phase.
- 3) The operating conditions are less severe for viscosity breaking than for thermal cracking because the visbreaker charge is heavier and more susceptible to decomposition, and the allowable conversion to gasoline is lower for viscosity breaking because of stability requirements of the products.

REACTIONS

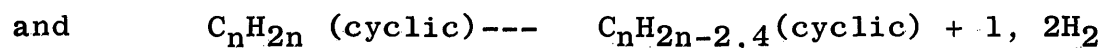
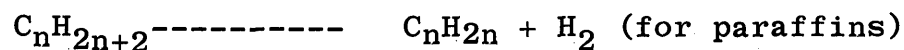
A literature survey relevant to the chemical transformations that occur during the thermal decomposition of hydrocarbons is presented here.

The reactions that occur during the thermal decomposition of hydrocarbons may conveniently be divided into two classes, designated as primary and secondary reactions.

A primary reaction, in general, is one in which the parent hydrocarbon is either in equilibrium with the decomposition products or forms nonreversible fragments.

Secondary reactions include all those which the products of a primary reaction undergo.

Two important primary reactions occur: equilibrium involving hydrogen, and irreversible splitting of the carbon to carbon bonds. For example, the equilibrium involving hydrogen can be represented by the general equations:



These equations are thermodynamically possible and have been shown to occur by numerous investigators (Frolich and Fulton, 1938, p. 2099).

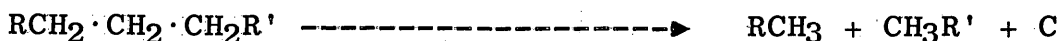
Splitting of the carbon to carbon bond is more likely to occur than the reaction involving hydrogen since the activation energy for the rupture of a carbon to carbon bond is about 71 kcal against 93 kcal for a carbon to hydrogen bond rupture; also there are indications of more complicated primary reactions (Rise, 1931, p. 1959).

The secondary reactions, embracing all those reactions which are generally termed as re cracking, differ from the primary reactions in definition only. In addition to these reactions, polymerization, together with the formation of branched olefins from other olefins, and cyclization reactions can occur under cracking conditions and are generally considered as secondary reactions.

Pyrolysis of paraffins

As a general rule it has been found (Frolich and Fulton, 1938, p. 2100) that paraffinic chains have the greatest tendency to crack in the temperature range covered by commercial liquid- and vapor-phase cracking

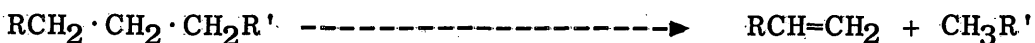
(750 to 1110°F); the rupture of the carbon to carbon bond can theoretically be considered to take place in three ways:



or



or



It has been shown that the rupture takes place exclusively according to the third reaction (Sachanen and Telicheyev, 1932, p. 94).

The first reaction is excluded due to the fact that the absence of carbon in the primary reaction products has been definitely proved.

The second reaction is excluded because the probability of this reaction's occurring is reduced in great extent by the high activation energy (91 kcal).

The points of rupture of normal paraffins in general seem to follow the law of chance, with all the theoretically possible complementary paraffins and olefins being found in the reaction products; in case of higher paraffins, the central carbon is the most susceptible to splitting. The same general rule of chance seems to hold true for the branched paraffins where any of the carbon to carbon bonds

of a primary, secondary, or tertiary carbon may break (Sachanen and Telicheyev, 1932, p. 110).

Pyrolysis of olefins

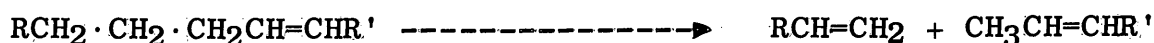
Although the occurrence of olefins in crude oil is insignificant (Frolich and Fulton, 1938, p. 2101), they play an important role in cracking since they are formed as one of the most important products of the primary reactions of paraffins and alkylated cyclics. Olefins, in general, are more resistant to heat than the corresponding paraffins (Hurd, 1934, p. 50).

Like paraffins, the stability of olefins decreases with increasing molecular weight; olefins may dehydrogenate to produce diolefins, but very little is known about the kinetics of this reaction, even for simple olefins. In general it is assumed to parallel the paraffin-to-olefin decomposition in the range of corresponding molecular weight.

When an olefin undergoes the carbon to carbon bond rupture, two courses are possible with the formation of either a paraffin and a diolefin, or two diolefins:

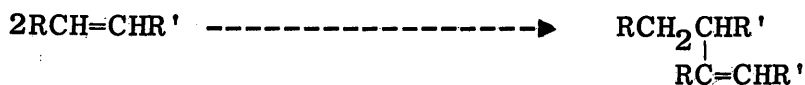


and



Indications are that for the lower cracking temperatures the formation of two olefins is the predominant reaction.

The most important role played by olefins in pyrolysis is their ability to polymerize into both cyclics and higher molecular weight olefins. Another type of polymerization occurring may be represented by the formation of a branched olefin from two simpler olefins:



More complex changes in structure usually occur.

Pyrolysis of aromatic hydrocarbons

The nucleus of aromatic hydrocarbons is considered to be stable in the range of temperature covered by commercial cracking, since excessive temperatures are required for the ring to open in the absence of a catalyst (Kinney, 1955, p. 133).

The remarkable thermal stability of aromatic hydrocarbons is demonstrated by the high temperature required for cracking of the heavy fractions of petroleum (800 to 1200°F) and of coal (500 to 2000°F). The stability is due to the unusually strong carbon to carbon bonds; the basis for the greater stability of these bonds in aromatic structures may be found in the fact that this structural arrangement

is related to the very stable structure of crystalline graphite, and the carbon to carbon bonds of the aliphatic hydrocarbons are similar to those less stable in the diamond crystal (Hurd, 1929, p. 15).

Pyrolysis of the mixed aromatic-aliphatic hydrocarbons

Alkylated aromatics. The thermal behavior of the alkylated aromatics is complicated by a multitude of reactions, all of which are affected by temperature, pressure, presence of hydrogen or other aromatics that may act as hydrogen acceptors, and olefins or other decomposition products; in addition to these, the longer side-chains or multiple substitutions increase the possibilities of more reactions (Kinney, 1955, p. 125).

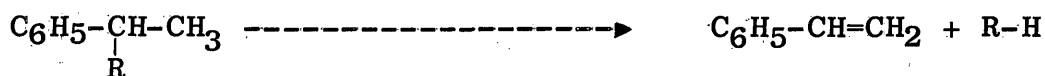
Despite the complexity of the product obtained, one point is clear: the stability of the aromatic ring system, which retains its identity through a great variety of pyrolytic reactions. One reaction, however, destroys the aromatic structure, and that is the pyrolysis in the presence of hydrogen, particularly in the presence of a catalyst which may serve as a hydrogenating agent. Under this condition, the aromatic rings are hydrogenated and then cracked; this type of decomposition frequently results in the formation of the unsubstituted aromatic which may undergo hydrogenolysis.

Cracking of the aliphatic side-chain. When alkylated aromatics are thermally cracked in the absence of an active catalyst, primary and secondary alkyl groups undergo extensive cracking within the side-chain, but tertiary groups undergo the dealkylation reaction. The generally applicable rules to the thermal decomposition of alkylated aromatics are:

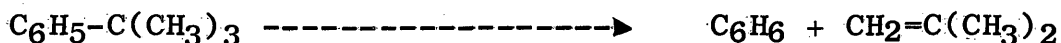
- 1) for primary alkyl groups



- 2) for secondary alkyl groups



- 3) for tertiary alkyl groups



Pyrolysis of hydrocarbon mixtures

In the cracking of petroleum, where any or all of the various classes of hydrocarbons are present, the course of the cracking reactions is governed in general by the relative stability of the various constituents, their reaction rates, and the equilibrium phenomena. Examination of the thermodynamic stability of hydrocarbons, as expressed by their free energy of formation from the elements, shows that all petroleum hydrocarbons, with the exception of

methane and possibly ethane, are potentially unstable at temperatures above 390°F; at lower temperatures and up to approximately 570°F the reaction rates are so low that no perceptible decomposition takes place, even in the case of the most unstable molecules. As temperature increases, the hydrocarbons, with the exception of acetylene, whose stability increases with temperature, become more and more unstable, each series having different temperature coefficients. Above 1110°F no hydrocarbon other than acetylene is thermodynamically stable with respect to the elements (Parks and Huffman, 1932, p. 101).

Such thermodynamic considerations lead to the important conclusion that with the temperatures employed in practice, the cracking of a hydrocarbon into smaller compounds is essentially a non-reversible process; on the other hand the reactions involving liberation of hydrogen are reversible.

While free energy relationships determine whether a certain type of reaction is possible, those reactions which do take place in cracking of a complex mixture of hydrocarbons are largely governed by relative reaction rates. In general it has been found that in the temperature range from 750 to 1110°F, the various classes of hydrocarbons may be listed as follows in order of increasing stability:

paraffins	C_nH_{2n+2}
olefins	C_nH_{2n}
diolefins	C_nH_{2n-2}
naphthenes (6 carbon nuclear)	C_nH_{2n} , C_nH_{2n-m}
naphthenes (5 carbon nuclear)	C_nH_{2n} , C_nH_{2n-m}
aromatics	C_nH_n

The stability of the higher members of any given series, with the exception of naphthenes, increases with decreasing ratio of hydrogen to carbon in the molecule, and it is a general rule that side-chains are somewhat more stable than the ends of straight chains. The relative order of stability outlined refers strictly to the temperature range specified.

At higher temperatures (1110° to 1290°F), diolefins become more stable than naphthenes, and it is possible by cracking at such high temperatures to convert naphthenes into diolefins, which in turn give aromatics by subsequent polymerization and liberation of hydrogen (Frolich, Simard and White, 1930, p. 240).

As the temperature of these complex hydrocarbon mixtures is increased in the cracking process, noticeable

decomposition usually takes place at temperatures above 570°F. This point of incipient cracking, however, is dependent not only upon temperature but also upon the nature of the most unstable hydrocarbons present in the charge stock. Beyond this point, the reaction rate doubles for an increment of 57°F at 840°F and gradually falls off to an increment of 70°F at 1110°F (Geniesse and Reuter, 1932, p. 219).

According to the relative stability of the hydrocarbons, it is apparent that the aliphatic hydrocarbons break first, followed by other types as the temperature is increased. As the temperature increases above 1290°F, more or less complete breakdown occurs, and it is characterized by excessive formation of coke and hydrogen; acetylene begins to appear at this stage.

There are widely different view points about the nature of petroleum coke and the mechanism of its formation, but it is believed that coke is mainly made up of free carbon or consists of highly condensed hydrocarbons.

The olefins resulting from the primary reactions, particularly those of high molecular weight, polymerize readily, and in this way new compounds are produced whose molecular weight tends to exceed that of the original stock. The unsaturated molecules possess less hydrogen,

on a carbon atom basis, than the original hydrocarbon; consequently the same holds for the polymerization product. On prolonged exposure to high temperatures, the polymerized materials undergo cracking, with the consequent formation of new unsaturated compounds which give rise to further polymerization. Progressive reactions of this type, along with condensation of the ring compounds, lead to the formation of more and more compounds of decreasing hydrogen to carbon ratio, and with this decrease the material becomes more refractory to temperature.

The final products are gaseous and low-boiling liquid compounds relatively high in hydrogen, and liquid reaction products of higher molecular weight, tar and petroleum coke, with a low ratio of hydrogen to carbon.

The complete cracking process is a sequence of decomposition and polymerization reactions, the character of the final products being determined by the nature of the hydrocarbons present in the original charge stock and by the temperature and pressure of the operation as well as the time of exposure to the cracking conditions.

Variables affecting the pyrolytic reactions

The controlling factors in a cracking operation have been found to be the reaction rate and the equilibrium

phenomena. Because of this, it is important to know the effect of time, temperature, and pressure on these factors.

Within narrow limits, time and temperature are practically interchangeable because a longer time at a lower temperature will bring about the same overall results as a higher temperature and a correspondingly shorter time. Beyond these limits there is a lower temperature where the hydrocarbon is stable and a higher temperature where the reaction cannot be controlled, no matter how short the contact time.

Temperature influences the course of the primary reactions to some extent and an increase in temperature increases the olefin content of the primary products, but the main effect of temperature is its influence on the velocity of reaction.

Pressure should have little influence on the velocity of reaction since the overall cracking reactions are calculated as being of the first order, but very high pressures probably lower the reaction rate. The pressure, however, does permit the use of higher temperatures by virtue of increasing the boiling point when liquid- or mixed-phase cracking is used; the increase in temperature aids in obtaining a higher velocity of reaction. Pressure also greatly influences the composition of the products of

cracking: low pressure favors a high gas to liquid product ratio; high pressure tends to depress the gas formation because of partial polymerization of gaseous olefins (Hugel and Artichevitch, 1928, p. 985).

DESIGN OF THE VISCOSITY BREAKING UNIT

One of the main objectives of this thesis was to determine the feasibility of applying a mild decomposition process to an aromatic extract from lubricating-oil processes. Viscosity breaking was chosen from the existing thermal processes because it is the only one characterized by the mild conditions of decomposition required by the theoretical support of the investigation.

The application of the viscosity breaking process is presented here in part through the design of a bench-scale reactor; this design is developed using the principles of operation of a commercial reactor; consequently it has to deal with two different but dependent points of view: process design and mechanical design.

Process design

The process characteristics for this project are determined basically by the properties of the material to

be treated and by the operations necessary to obtain the transformation of the oil; the required operations are:

- 1) the oil is preheated to a temperature close to the desired operation range and is supplied with the required heat of decomposition;
- 2) the oil is quenched in order to stop the cracking reaction;
- 3) the pressure used to keep the oil in the liquid-phase is released, and the lighter fractions are flashed overhead in a flash drum;
- 4) the light products are cooled and the gas- and liquid-phases are separated in a drum;
- 5) the heavy products are cooled.

The temperature range of operation and the energy requirements for preheating and decomposition are obtained from some of the physical properties and the thermal characteristics of the aromatic extract together with a material balance of the process.

The data about physical properties and thermal characteristics is obtained from laboratory tests and from generalized charts and procedures available for this purpose. The material balance is obtained from the prediction of yield by viscosity breaking.

The prediction of the yield by viscosity breaking includes the following calculations (Nelson, 1958, p. 640): minimum gravity of the cracked product; yield of light cracked product; unaccounted for loss; increase in total liquid yield; and estimation of the gas production.

Viscosity breaking being a mild cracking process, the decomposition reactions are endothermic; consequently with the information obtained from the material balance and some thermal characteristics of the aromatic extract, it is possible to calculate the energy requirements for decomposition (Nelson, 1958, p. 633).

The calculation of the minimum surface required for preheating is based on the flow rate of oil, the operation temperature, the thermal characteristics of the oil, and the heat transfer coefficient of this section of the apparatus.

The heat of decomposition is supplied using a pipe-coil in an isothermal salt bath; consequently the design of the reactor is based on the determination of the heating surface required to supply a given amount of energy at a constant temperature and at a given conversion. For a first order reaction and a system of these same characteristics Walas (1959, p. 75) gives the following formula:

$$A = \frac{k (n_{a0} - x) \Delta H_r}{U (T_m - T)} \text{ sq ft}$$

where:

A is maximum surface needed (sq ft)

k is reaction velocity constant (hr)

n_{a0} is weight feed (lb)

U is overall heat transfer coefficient (Btu/hr-sq ft-°F)

ΔH_r is heat of reaction (Btu/lb)

T_m is temperature of the heating media (°F)

T is temperature of reaction (°F)

x is conversion (lb)

Viscosity breaking is a first order reaction like cracking; consequently the expression for the reaction velocity constant is the same as for cracking but modified to fit the viscosity breaking reaction (Cooper and Ballard, 1962, p. 217):

$$k = \frac{1}{t} \ln \frac{100}{X}$$

where:

k is first-order reaction velocity constant (1/sec)

t is residence time based on charge liquid volume (sec)

X is volume % distilled at 900°F, plus viscosity broken residuum volume %.

The quenching operation is performed by cooling the effluent stream from the reactor in a tubular water cooler, and the temperature of the viscosity broken stream is controlled by changing the flow rate of the cooling agent; the design of this water cooler is based on the temperature of the viscosity broken products and the heat transfer coefficient of the system.

The flashing of the products is obtained on a drum whose design is based on the critical velocity of the mixed-phase stream, so that the vapor phase separated is free from liquid entrainment. The critical velocity depends basically on the densities of the two phases.

The vapor phase overhead of the flash drum is cooled, and the condensed product is separated from the noncondensable gas by means of a separation drum. The condenser-cooler design is based on the dew points of the expected components of the liquid phase, and the separation drum is designed using the same principle of critical velocity of the mixed-phase stream as for the flash drum.

The liquid bottoms of the flash drum are cooled in a tubular exchanger, designed so the temperature of the product may be controlled by variation of the flow rate of the cooling agent.

The isothermal salt baths are taken to the operation temperature by means of radiant gas burners. The number of burners required is determined from the heating capacity of the gas combustible, the capacity of the individual burners, and the total energy that must be supplied for the operation.

The total energy to be supplied includes the pre-heating energy, the energy of decomposition, the heat lost with the flue gases, and the energy required for heating the system in a reasonable time (two or three hours).

The small surface provided by the containers of the salt baths and the relatively large amount of energy to be supplied to the system give a high thermal density which makes it imperative to use radiant burners.

Mechanical design

The mechanical design considers three aspects:

- a) the strength of materials for the temperature and pressure levels of operation;
- b) the availability of the materials to be used, including standard sizes and chemical composition; and
- c) the problems related to the construction of the equipment.

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of three parts:

- 1) determination of properties and characteristics of the aromatic feed stock;
- 2) design of the viscosity breaking experiments; and
- 3) determination of properties and characteristics of the viscosity broken products.

Determination of properties and characteristics of the aromatic feed stock

The aromatic extract used in this investigation was 170 Pale Oil supplied by Continental Oil Company.

The properties of this oil were determined using the following tests (ASTM, 1958, p. 8-720):

- a) API gravity, specific gravity, and density by methods ASTM D-282 and ASTM D-1298;
- b) Saybolt universal viscosity, kinematic viscosity, and viscosity index by methods ASTM D-88, ASTM D-445, and ASTM D-567;

- c) Refractive index and refractive dispersion by method ASTM D-1218;
- d) Distillation by methods ASTM D-158 and ASTM D-86;
- e) Aniline point and mixed aniline point by method ASTM D-611; and
- f) Bromine number by method ASTM D-1158.

The thermal characteristics of the feed stock were determined using the data obtained from the distillation test together with existing correlations, as follows:

- a) average boiling points (Maxwell, 1960, p. 15);
- b) characterization factor (Maxwell, 1960, p. 16);
- c) molecular weight (Maxwell, 1960, p. 21);
- d) atmospheric equilibrium flash vaporization (Maxwell, 1960, p. 222-229); and
- e) flash vaporization at higher pressures (Maxwell, 1960, p. 222-229).

The results of the tests and determination of characteristics are presented in table 1.

TABLE 1PROPERTIES AND CHARACTERISTICS OF
170 PALE OIL FURFURAL EXTRACT

Gravity °API at 60°F	15.6
Specific gravity at 60°F	0.9619
Density at 60°F lb/gal	8.011
Viscosity: Saybolt universal sec at 100°F	550
Saybolt universal sec at 130°F	172
Saybolt universal sec at 210°F	45
Kinematic cs at 100°F	119
Kinematic cs at 130°F	36.5
Kinematic cs at 210°F	5.7
Viscosity index	-321
Refractive index at 21.5°C	1.5440
Refractive dispersion at 21.5°C	309
Aniline point °F	112
Mixed aniline point °F	125
Bromine number	48.1
Distillation ASTM D-158 at 760 mm Hg	°F
IBP	701
10%	713
20%	722
30%	730
30%	739
40%	747
60%	754
70%	761
80%	778
90%	794

TABLE 1 continued

Volume average boiling point	°F	750
Weight average boiling point	°F	766
Mean average boiling point	°F	764
Molal average boiling point	°F	766

Equilibrium flash vaporization at several pressures

Vaporized %	1 atm °F	2 atm °F	3 atm °F	4 atm °F
5	766	833	877	908
10	769	836	881	912
20	774	841	885	916
30	779	846	889	919
40	783	850	892	922
50	787	854	895	925
60	792	859	898	928
70	795	862	901	930
80	801	868	905	934

The graphical representation of the distillation is given in figure 1.

The graphical representation of the equilibrium flash vaporization at several pressures is given by figure 2.

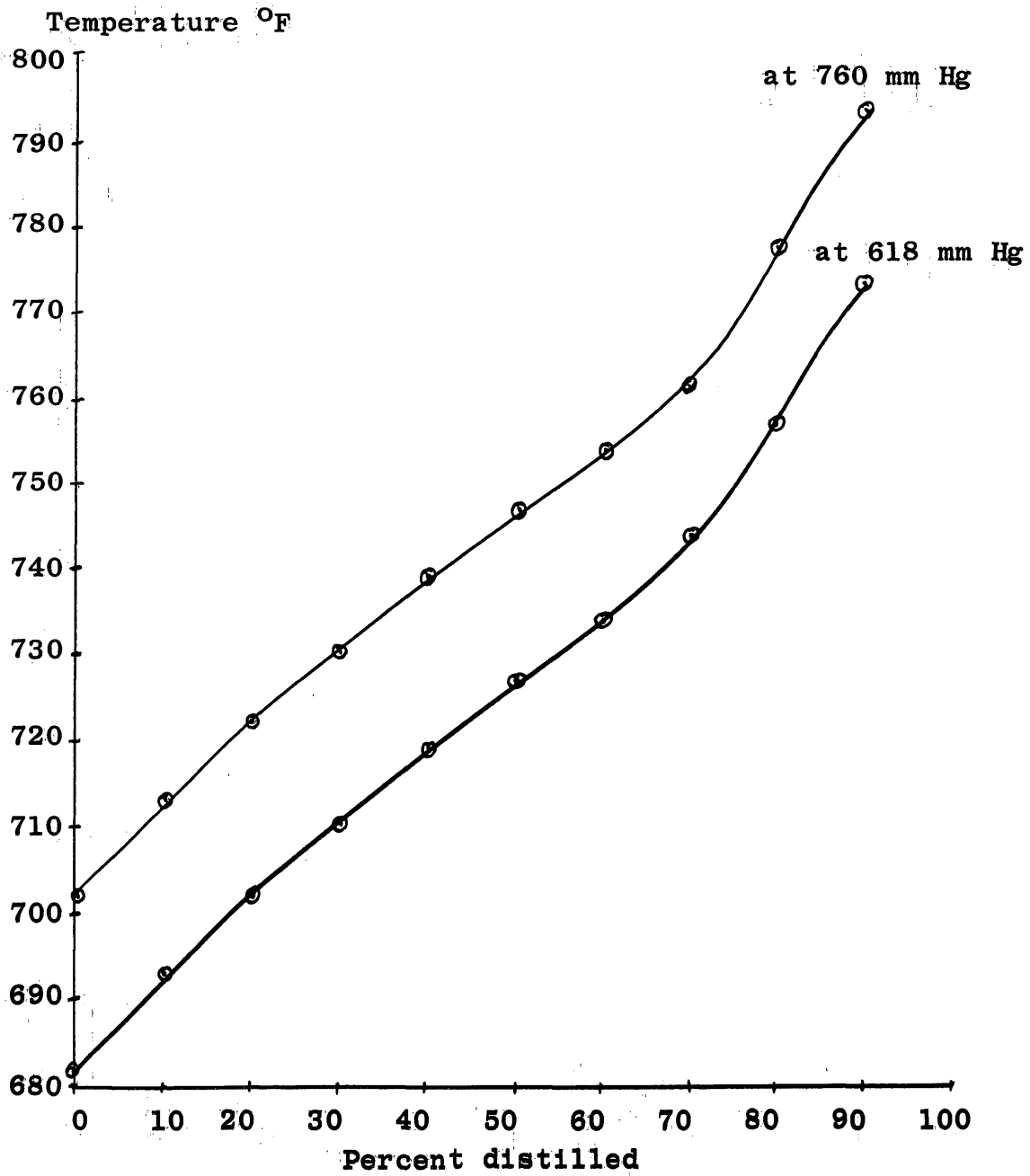
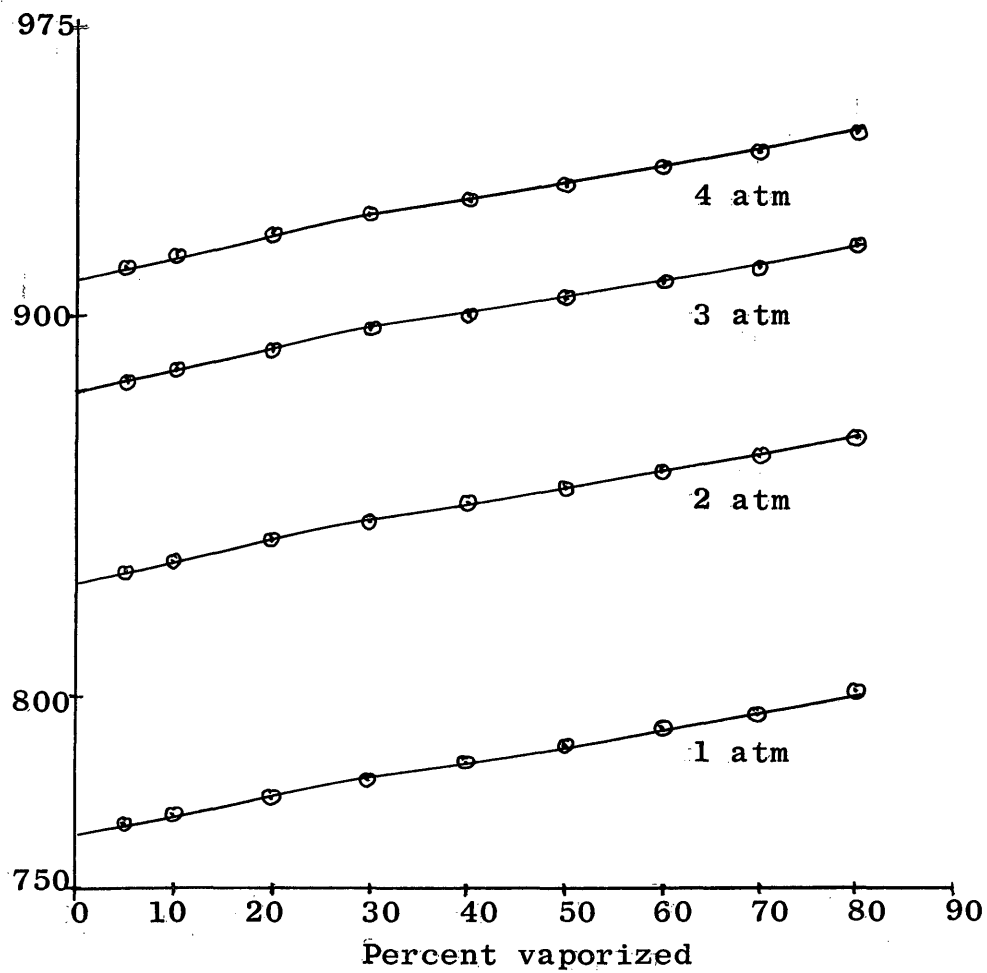
FIGURE 1DISTILLATION ASTM D-158 OF 170 PALE-OIL FURFURAL EXTRACT

FIGURE 2

EQUILIBRIUM FLASH VAPORIZATION OF 170 PALE-OIL
FURFURAL EXTRACT AT SEVERAL PRESSURES

Temperature °F



Design of the viscosity breaking experiments

The viscosity breaking experiments were planned according to the following program:

As there was no indication of previous investigations in this area, it was decided to start the exploration for viscosity breaking conditions (temperature, pressure, and reaction velocity constant) at the lowest temperature range possible. The lowest temperature is given by the initial boiling point, at atmospheric pressure, of the aromatic extract; from this point the temperature and pressure should be increased progressively up to a point close to the critical point of the oil, so as to keep the stock in the liquid phase.

The zone to explore was found to be between 700 and 1100°F, with pressures between 15 and 250 psi.

The experimental procedure for the viscosity breaking experiments consisted basically of the same procedure used in commercial plants, that is, the oil was preheated to the desired temperature, and supplied with the heat of decomposition, keeping the stock in the liquid phase using the pressure corresponding to the temperature of operation as indicated by the flash vaporization at several pressures (see figure 2).

The outlet stream from the reactor was quenched down to 700°F, the pressure released and the viscosity-broken stream was flashed. The light portion overhead of the flash drum was cooled, and the liquid condensed was separated from the noncondensable gases in a separation drum; the gases were measured and burned; the condensate was measured and collected for laboratory tests; the bottoms of the flash drum were cooled, measured and collected for laboratory tests.

During each experiment, samples were taken when conditions of temperature and pressure changed.

Determination of properties and characteristics
of the viscosity broken products

The viscosity broken products and the samples taken on each experiment were tested using the same methods as for the aromatic extract.

EXPERIMENTAL DATA AND RESULTS OF LABORATORY TESTS

The experimental data and results of the laboratory tests are presented here in three parts:

- 1) identification of the products and samples taken during the experiment;
- 2) experimental data obtained during the viscosity breaking operation; and
- 3) results of the laboratory tests on the products and samples.

Identification of the products and samples

The identification of the products obtained and samples taken from the viscosity breaking experiment is presented in table 2. The identification of the samples is presented by indicating the temperature and pressure conditions at which the samples were taken and the stream from which they were taken.

Experimental data obtained during the
viscosity breaking operation

The experimental data obtained during the viscosity breaking operation are presented in table 3.

The material balance calculated from these experimental data is presented in table 4.

Results of the laboratory tests

- a) The results obtained on API gravity, specific gravity, and density are presented in table 5.
- b) The results obtained on Saybolt universal viscosity, kinematic viscosity, and viscosity index are presented in table 6.
- c) The results obtained on refractive index and refractive dispersion are presented in table 7.
- d) The results obtained on distillation are presented in table 8.
- e) The results obtained on aniline point and mixed aniline point are presented in table 9.
- f) The results obtained on bromine number are presented in table 10.

TABLE 2IDENTIFICATION OF SAMPLES AND PRODUCTS

<u>Name given to</u> <u>sample or product</u>	<u>Identification</u>
Light Product	mixture of all the overhead product of the flash drum collected during all the viscosity breaking operation.
Heavy Product	mixture of all the bottoms product of the flash drum collected during all the viscosity breaking operation.
Sample 1-L	sample of the overhead of the flash drum taken when the pressure in the coil was 40 psi, and the temperature of the oil was 750°F.
Sample 1-H	sample of the bottoms of the flash drum taken at the same conditions of sample 1-L.
Sample 2-L	sample of the overhead of the flash drum taken when the pressure in the coil was 110 psi, and the temperature of the oil was 700°F.
Sample 2-H	sample of the bottoms of the flash drum taken at the same conditions of sample 2-L.
Sample 3-L	sample of the overhead of the flash drum taken when the pressure in the coil was 120 psi, and the temperature of the oil was 800°F.
Sample 3-H	sample of the bottoms of the flash drum taken at the same conditions of sample 3-L.

TABLE 3EXPERIMENTAL DATA OBTAINED DURING
THE VISCOSITY BREAKING OPERATION

Feed to the unit	1 gal (8.011 lb)
Light product obtained	1100 ml (2.02 lb)
Heavy product obtained	2250 ml (4.89 lb)
Gas produced (35 mol. wt) wet	6.93 cu ft at 80°F
Time of operation (approx)	45 min
Flow rate	1.33 gal/hr
Temperature range of operation	700 to 800°F
Pressure range of operation	40 to 120 psi
Time of contact (theoretical)	1060 sec
Length of preheater coil	8 ft, 1/4 in nominal diam
Length of reactor coil	72 ft, 1/4 in nominal diam
Reaction velocity constant	0.00049 sec ⁻¹
Conversion obtained	29% by volume

The experiment had to be stopped because of excessive coke formation.

TABLE 4MATERIAL BALANCE OF THE VISCOSITY BREAKING OPERATION

	Balance obtained			Balance Predicted		
	°API	lb	wt %	°API	lb	wt %
Feed	15.6	8.02	100	15.6	8.02	100
Light Product	37.5	2.02	25.5	56	2.20	27.4
Heavy Product	11.6	4.89	60.9	2	5.94	61.6
Gas (35 mol wt)		0.64	8.0		0.32	4.0
Loss and Coke		0.47	5.9		0.56	7.0

TABLE 5API GRAVITY, SPECIFIC GRAVITY, AND DENSITY OF THE PRODUCTS

	^o API at 60°F	Specific Gravity 60°F/60°F	Density lb/gal at 60°F
170 Pale oil	15.6	0.9619	8.011
Light Product	37.5	0.8373	6.792
Sample 1-L	44.3	0.8047	6.701
Sample 2-L	32.5	0.8628	7.184
Sample 3-L	30.1	0.8759	7.291
Heavy Product	11.6	0.9888	8.235
Sample 1-H	14.2	0.9712	8.088
Sample 2-H	7.9	1.0151	8.454
Sample 3-H	3.0	1.0521	8.762

TABLE 6VISCOSITY AND VISCOSITY INDEX OF THE PRODUCTS

	Saybolt universal seconds			Kinematic Viscosity centistokes		
	100°F	130°F	210°F	100°F	130°F	210°F
170 Pale Oil	550	172	45	119	36.5	5.7
Light Product	-	-	-	1.25	0.98	0.59
Sample 1-L	-	-	-	0.96	0.80	0.54
Sample 2-L	-	-	-	1.29	1.02	0.62
Sample 3-L	-	-	-	1.30	1.03	0.65
Heavy Product	139	74	39.5	29.5	23.2	14.0
Sample 1-H	160	85	42	34.2	17	4.8
Sample 2-H	92	57	37	18.6	9.8	3.2
Sample 3-H	127	57	33.5	26.7	9.8	2.2

TABLE 7REFRACTIVE INDEX AND REFRACTIVE DISPERSION OF THE PRODUCTS

	Temperature °C	n _D	(n _F -n _C) x 10 ⁴
170 Pale Oil	21.5	1.5440	309
Light Product	21.0	1.4839	171.1
Sample 1-L	21.0	1.4681	41.4
Sample 2-L	21.0	1.5088	253.7
Sample 3-L	20.5	1.5171	293.3
Heavy Product	21.0	1.5562	396
Sample 1-H	21.0	1.5605	334.4
Sample 2-H	20.5	1.6088	406.5
Sample 3-H	20.5	1.6301	406

TABLE 8DISTILLATION AND CHARACTERISTICS OF THE PRODUCTS

	ASTM D-158 Pale Oil	ASTM D-86 Light Product	ASTM D-158 Heavy Product	ASTM D-158 Sample 1-H	ASTM D-158 Sample 2-H
	°F	°F	°F	°F	°F
IBP	681	135	255	265	220
10%	693	185	505	540	400
20%	702	239	628	668	560
30%	710	289	666	698	642
40%	719	341	677	712	682
50%	727	392	683	730	712
60%	734	435	691	742	735
70%	744	501	cracking	743	cracking
80%	757	cracking		cracking	
90%	774				

see figure 3

	170 Pale Oil	Light Product	Heavy Product
Correlation Index	20.7	25.3	32.4
Characterization Factor	11.1	10.9	10.5
Molecular Weight	325	122	256
Mean Average Boiling Point °F	764	302	681

Note: all distillation data are at 618 mm Hg

FIGURE 3

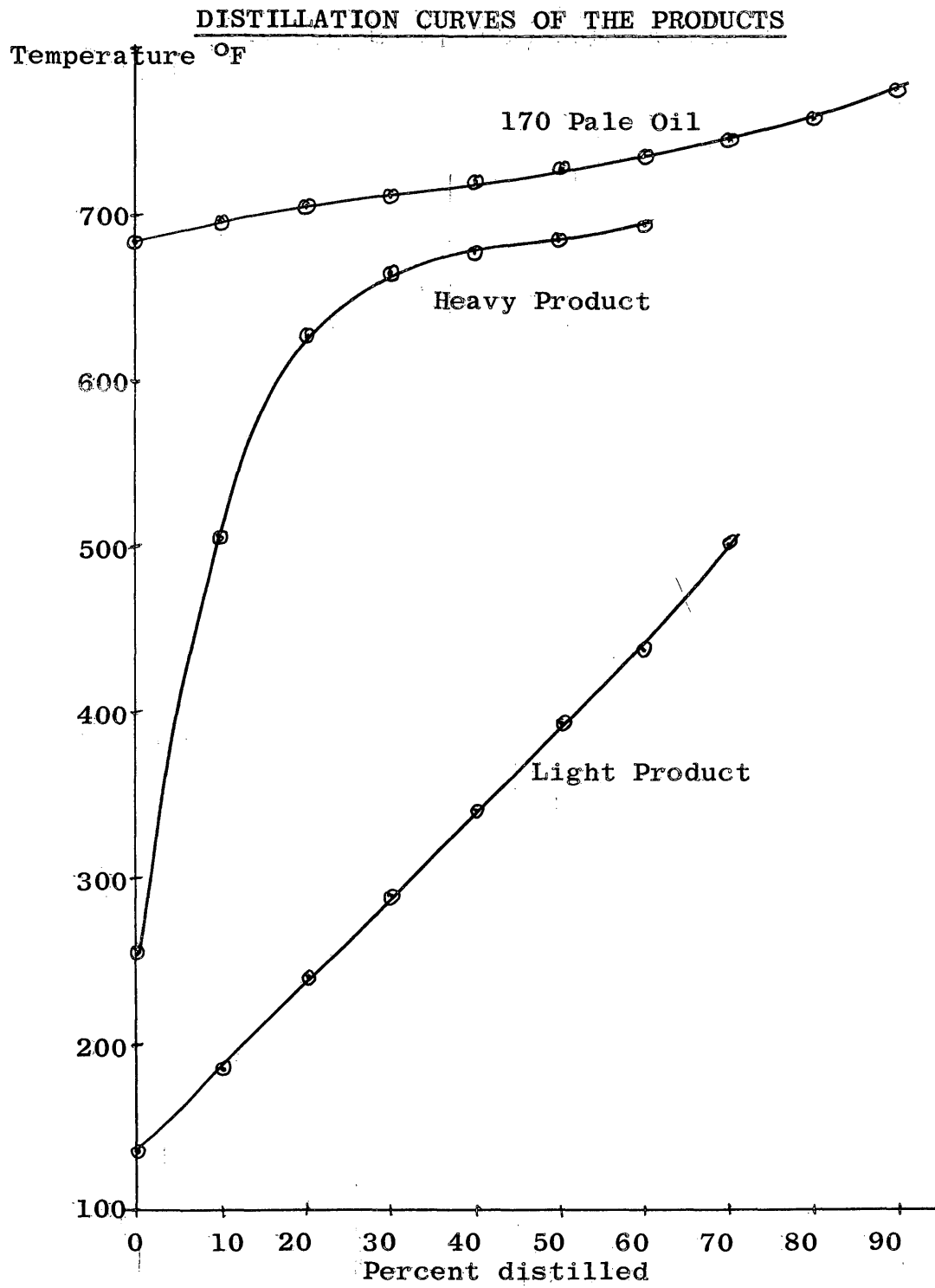


TABLE 9ANILINE POINT AND MIXED ANILINE POINT OF THE PRODUCTS

	Aniline Point °F	Mixed Aniline Point °F
170 Pale Oil	112	125
Light Product	-	102
Sample 1-L	-	-
Sample 2-L	-	99
Sample 3-L	-	94
Heavy Product	62	108
Sample 1-H	79	113
Sample 2-H	56	90.5
Sample 3-H	-	80.5

TABLE 10BROMINE NUMBER OF THE PRODUCTS

	Bromine Number
170 Pale Oil	48.1
Light Product	55
Sample 1-L	-
Sample 2-L	56.6
Sample 3-L	60.1
Heavy Product	27.2
Sample 1-H	22.4
Sample 2-H	27.5
Sample 3-H	34.2

DISCUSSION OF RESULTS

The discussion of the results is presented here in two parts:

- 1) interpretation of the experimental data obtained from the viscosity breaking experiment; and
- 2) discussion of the results of the physical and chemical tests.

Interpretation of the experimental data from the viscosity breaking operation

At the earlier stages of the investigation, it was thought that decomposition would take place about 1050°F, or the upper levels of the temperature range to explore (700 - 1100°F), but the results presented in table 3 indicate beyond any doubt that the decomposition can be easily obtained at the lower levels of the range, 650 - 750°F.

The data obtained during the experiment also show that the formula used for the design of the reactor coil

(Walas, 1960, p. 75), can be applied to this type of system within an acceptable margin of error.

In general, the experimental data obtained from the operation, supply a practical proof for two of the basic assumptions of this investigation:

- 1) the relatively low temperature required to obtain decomposition is an indication of the presence of aromatic-aliphatic hydrocarbons in the aromatic extract;
- 2) the moderate operating conditions used are a proof of the assumption that the aromatic-aliphatic hydrocarbons can be partially transformed by viscosity breaking techniques.

The material balances presented in table 4 indicate that the yields obtained correspond closely to the predicted, with two exceptions:

- a) the amount of gas produced in the decomposition was twice as great as predicted; and
- b) the API gravities of the products obtained were considerably different from the predicted ones.

The general statement that viscosity breaking is a noncoking process cannot be applied to this experiment; this is indicated by the fact that the operation had to be stopped after 45 minutes because excessive coke formed

in the coils. This is a fact that must be carefully considered in the design of the reactor coil in future investigations in this area.

Discussion of the results of the physical and chemical tests

The interpretation of the results of each of the physical and chemical tests is presented here:

1) the results of the gravities and density determinations (see table 5) indicate that the light product is considerably lighter than the aromatic extract, and that the heavy product is just heavier than the feed stock.

The API gravities of the samples 1-L, 2-L, 3-L, and 1-H, 2-H, 3-H show that this physical property changes with the temperature and pressure of operation, with the best results obtained at the milder conditions. It is clear that the gravity changes inversely with the severity of operation conditions.

2) The results obtained in the viscosity tests (see table 6), tend to prove the third basic assumption of this investigation: that the high viscosity of the aromatic extract is caused, at least partially, by the complex structure of the aromatic-aliphatic hydrocarbons.

The notable changes of viscosity obtained, not only for the light product but also for the heavy one, are

clear demonstrations of the effectiveness of the viscosity breaking process when it is applied to decomposition of this aromatic extract. It is also clear that the viscosity changes inversely with the severity of operation conditions.

- 3) The results obtained in the calculations for refractive dispersion (see table 7), indicate that although the aromatic character of the products is kept, the light product is more unsaturated than the heavy product (Sachanen, 1945, 109).
- 4) The results obtained in the distillation tests (see table 8) give clear indication of the improvement obtained in volatility for the two viscosity broken products.

From the characteristics calculated, the correlation index indicates that the original aromatic extract contains hydrocarbons with paraffinic side-chains (correlation index less than 25). The 25.3 correlation index of the light product indicates that the aromatic character is compensated by the paraffinic side-chains. For the heavy product, with a correlation index of 32.4, the indication is that the aromatic character of the hydrocarbons is increased (Sachanen, 1945, p. 418). The molecular weight of the light product was calculated as 122; this indicates that the molecular structure of the aromatic hydrocarbons in

this product is that of hydrocarbons of one aromatic ring with attached olephinic side-chains.

- 5) The results obtained in the mixed aniline point determinations (see table 9) indicate that, as assumed originally, the decomposition takes place basically on the aliphatic portion of the aromatic-aliphatic hydrocarbons. This statement is supported by the fact that the mixed aniline point of the two products was lower than that of the aromatic extract; consequently the aromatic character of the products is stronger than that of the feed stock, as indicated by the significance of the test (ASTM, 1957, p. 74).

Apparently the influence of the change in molecular weight over the aniline point is compensated in part by the improvement of the aromatic character of the products (ASTM, 1957, p. 74). The mixed aniline point of the samples indicates that the aromatic character changes directly with the severity of decomposition.

With the statement of improvement of aromatic character the author intends to express the decrease in size of the aliphatic chains attached to the aromatic rings: this concept is also based on the

significance of the aniline point test, which indicates that the aniline point of aromatics and naphthenes is lower than that of paraffins (ASTM, 1957, p. 74).

- 6) The results obtained in the bromine number test (see table 10) indicate that the content of bromine-reactive constituents of the light product is larger than that of the aromatic extract. The content of bromine-reactive constituents in the heavy product is considerably smaller than that in the aromatic extract, as indicated by the reduction in bromine number (ASTM, 1957, p. 101). The bromine number obtained for the samples indicates that the content of bromine-reactive constituents changes inversely with the severity of decomposition.

CONCLUSIONS

This investigation has established two main conclusions:

- 1) The transformation of aromatic extracts from lubricating-oil processes is possible using a mild decomposition process under operation conditions of temperature 700 to 800°F; pressure 40 to 120 psi, and residence time of the order of magnitude of 1000 sec.
- 2) The viscosity breaking effectively reduced the viscosity from 119 cs at 100°F to 1.25 cs at 100°F for the light product, and to 29.5 cs at 100°F for the heavy product. The volatility of the original stock was also increased as is indicated by the change in average boiling points: from 764°F for the aromatic extract to 302°F for the light product and to 681°F for the heavy product.

RECOMMENDATIONS

The author has two recommendations for future work:

- 1) Continue the investigation of application of viscosity breaking for the transformation of aromatic extracts preferably at the lower range of temperature and pressure used in this investigation (approximately 650°F, 50 psi, and time of contact about 200 sec).

The design of the reactor coil must be corrected for a yield of about 25% by weight; the technical problem presented by the large rate of coke formation must be carefully considered.

- 2) The investigation of the properties and characteristics of the light product must be extended to find its application as solvent for the chemicals used as preservatives and pesticides in the wood industry.

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APPENDIXSAMPLE CALCULATIONS FOR DESIGN
OF THE VISCOSITY BREAKING APPARATUS

Yield by viscosity breaking (Nelson, 1958, p. 640)

Gravity of stock = 15.5 °API

Specific gravity = 0.962

Density = 8.02 lb/gal

Characterization factor = 11.2

a) assuming that the stock is to be viscosity broken as severely as possible, the approximate minimum gravity of the cracked residue possible by severe thermal cracking of heavy residual hydrocarbons is 2.0 °API (Nelson, 1958, p. 639, table 19-6);

b) this decrease in gravity results in a yield of light cracked product (Nelson, 1958, p. 637, equation 19-1)

$$\% \text{ light cracked product} = 4 + 2(A_D - A_F)$$

$$A_D = 15.5 \text{ °API}$$

$$A_F = 2.0 \text{ °API}$$

$$\% \text{ light cracked product} = 4 + 2(15.5 - 2.0) = 31\%$$

from Nelson (1958, p. 638, fig. 19-1) the yield of light product is 40% vol;

c) the unaccounted for loss (Nelson, 1958, p. 638, equation 19-4) is:

$$\text{Liquid volume loss} = 0.5(A_D - A_F) = 7\% ;$$

- d) the average gas production on viscosity breaking can be assumed as 4%;
- e) the increase in total liquid yield is assumed as 5%; consequently the total liquid yield is 105% vol.;
- f) a material balance based on 1 gal of feed shows:

Feed (15.5 °API) = 1.0 x 8.02 =		8.02 lb
Light product (56 °API) = 0.35 x 6.283 =	2.200 lb	
Gas = 0.04 x 8.02 =	0.321 lb	
Unaccounted for loss = 0.07 x 8.02	<u>0.563 lb</u>	
	3.084 lb	<u>3.08 lb</u>

Weight of heavy residue and gas-oil 4.94 lb ;

- g) the amount of excess gas-oil above that required to reduce the viscosity of the heavy residue will be "x" % of 20 °API material (assumed)

$$4.94 = 7.78x + 8.84(1.05 - 0.35 - x) \quad x = 1.17\%$$

- h) the yield is:

1) by weight

	lb	wt %
Light product (gasoline, gas, and loss)	3.08	38.4
Gas-oil (20 °API)	0.10	1.5
Heavy residue (2 °API)	<u>4.84</u>	<u>60.1</u>
	8.02	100.0

2) by volume

Light product	35%
Gas-oil	1%
Heavy residue	<u>69%</u>
Total liquids	105%

Heat of decomposition (Nelson, 1958, p. 633)

a) one pound of this material is viscosity broken to produce:

Gas (gas + loss)(fixed)	11%
Gasoline	27%
Tar (cracked)	62%

b) the properties of these materials are:

Material	Characterization factor	°API	Heat of combustion Btu/lb
Feed	11.2	15.5	18,600
Gas	12		22,150
Gasoline	11.2	56	20,160
Tar	10.2	2	17,820

c) the heat of decomposition at 60°F is:

Basis = 1 lb

Energy in stock = 1(-18,600) = -18,600 Btu

Energy in products:

Heat in gas = 0.11(-22,150) = - 2,440 Btu

Heat in gasoline = 0.27(-20,160) = - 5,440 Btu

Heat in tar = 0.62(-17,820) = -11,050 Btu

subtracting -18,930 Btu -(-18,930)Btu

+ 330 Btu

Heat of decomposition at 60°F = 330 Btu/lb

d) the heat of decomposition at 1100°F is:

from Nelson (1958, p. 170, fig. 5-3)

sensible heat of gas at 1100°F 880 Btu/lb

sensible heat of gasoline at 1100°F 795 Btu/lb

sensible heat of tar at 1100°F 725 Btu/lb

then:

Cool stock from 1100°F to 60°F

$$1(60 - 1100) 0.628 = - 665 \text{ Btu}$$

Decomposition at 60°F + 330 Btu

Heat gas at 1100°F = 0.11(880) + 97 Btu

Heat gasoline at 1100°F =

$$0.27(795) \qquad \qquad \qquad + 214 \text{ Btu}$$

Heat tar at 1100°F = 0.62(725) + 450 Btu

$$\qquad \qquad \qquad +1091 \text{ Btu} \qquad \qquad \underline{+1091 \text{ Btu}}$$

difference in energy (heat absorbed) (adding) + 426 Btu

Heat of decomposition at 1100°F = 426 Btu/lb

Design of the reactor

a) The total energy required for decomposition at 1100°F

using a flow rate of 2 gal/hr is:

$$Q = 2(8.02)426 = 6830 \text{ Btu/hr}$$

the energy required for preheating the oil from 60°F to 1100°F is not accounted for here because the oil is preheated in a separated unit.

- b) The reaction velocity constant is obtained from the modified expression for viscosity breaking (Cooper and Ballard, 1962, p. 217):

$$k = \frac{1}{t} \ln \frac{100}{X}$$

for this case:

$$t = 150 \text{ sec (Nelson, 1958, p. 654)}$$

$$X = 69\%$$

then:

$$k = 1/150 \ln 100/69 = 0.0015 \text{ sec}^{-1}$$

- c) Heat transfer coefficients:

the tube heat transfer coefficient was calculated by the method of Buthod and Whiteley (1944, p. 2); the result obtained was $h_1 = 2400 \text{ Btu/hr-sq ft-}^\circ\text{F}$

the oil-film heat transfer coefficient was determined by using the method presented by Maxwell (1960, p. 211); the result obtained was $h_2 = 56 \text{ Btu/hr-sq ft-}^\circ\text{F}$

the overall heat transfer coefficient obtained was 55 Btu/hr-sq ft- $^\circ\text{F}$

- d) Reactor heat transfer surface:

for an isothermal salt bath Walas (1959, p. 75) gives the following formula:

$$A = \frac{k (n_{a0} - x) \Delta H_r}{U(T_m - T)} \text{ sq ft}$$

in this case: $k = 0.0015 \text{ sec}^{-1} = 5.4 \text{ hr}^{-1}$

$$n_{a0} = 16 \text{ lb}$$

$$\Delta H_r = 426 \text{ Btu/lb}$$

$$x = 0 \text{ (for maximum surface)}$$

$$U = 55 \text{ Btu/hr-sq ft-}^\circ\text{F}$$

$$T = 1100^\circ\text{F}$$

$$T_m = 1200^\circ\text{F}$$

$$A = 6.66 \text{ sq ft}$$

the inside area of 1/4 in tube is 0.0954 sq ft/ft

then the required length of tube is $6.66/0.0954 = 70 \text{ ft}$.

The general layout of the viscosity breaking apparatus is presented in figure 4.

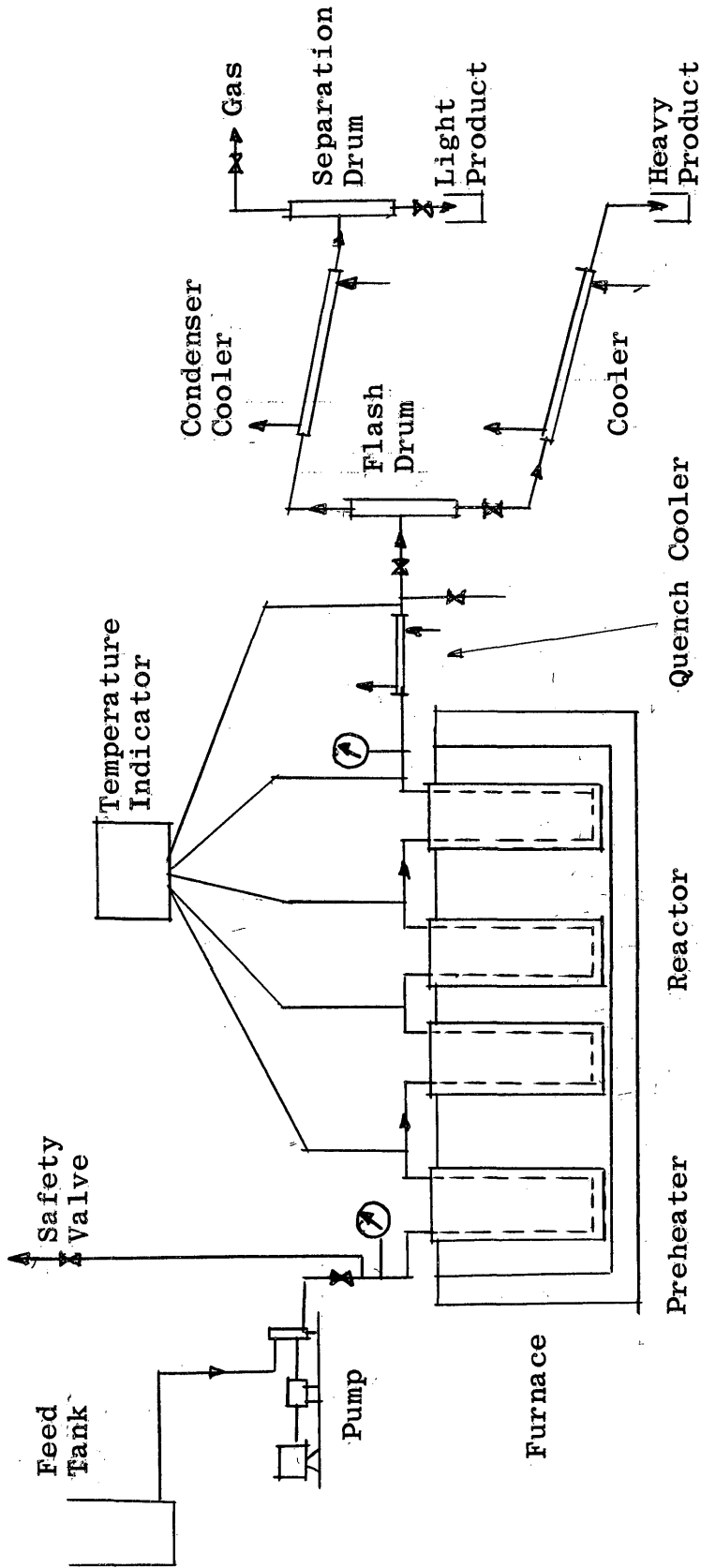


FIGURE 4

GENERAL LAYOUT OF THE VISCOSITY BREAKING APPARATUS