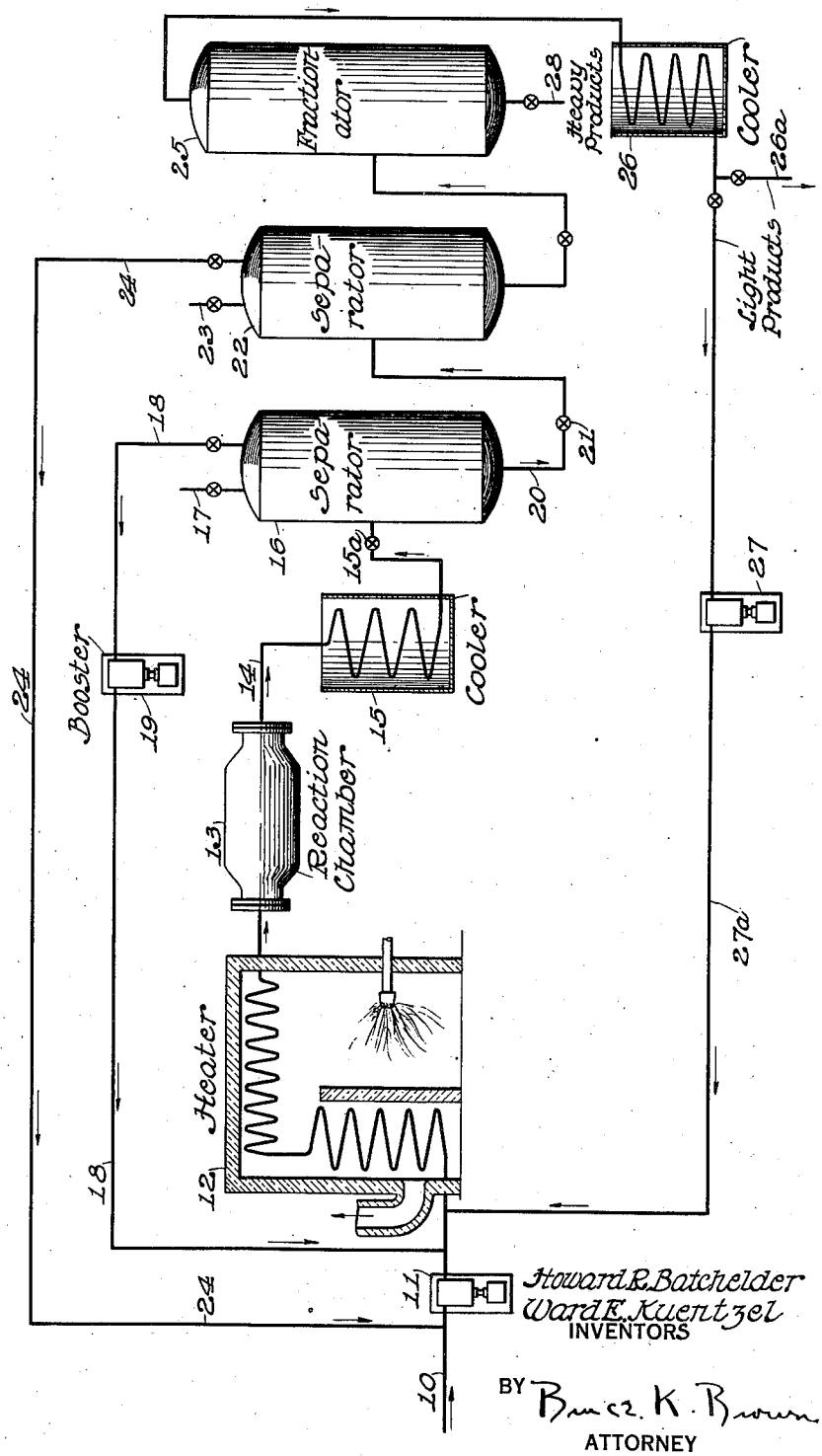
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PRODUCTION OF IMPROVED LUBRICATING OILS

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PRODUCTION OF IMPROVED LUBRICATING OILS

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9 Claims. (Cl. 196—10)

Our process relates to the production of improved lubricating oils by the high pressure polymerization of gaseous olefins.

It is well known that gaseous olefins may be polymerized at elevated temperatures and pressures to yield liquids ranging from gasoline-type products to extremely high boiling and viscous oils, depending on the temperatures, pressures and catalysts used. Previous investigators have, however, reported that lubricating oils produced by such methods have highly undesirable characteristics, in particular displaying very undesirable temperature-viscosity relationships.

The temperature viscosity characteristics of lubricating oils are best compared and defined by the so-called Dean and Davis Viscosity Index (see Dean and Davis, Chem. Met. Eng. Vol. 36, page 618, 1929) (abbreviated herein as V. I.). According to this criterion, the higher the V. I. the less the change of the viscosity of the oil with change in temperature, a low rate of such change (i. e. a high V. I.) being a highly desirable characteristic of lubricating oils. The highest V. I. found among oils derived by distillation from naturally occurring crude oils is approximately 100, while the V. I. of lubricating oils from low grade crude oils is in the vicinity of 20.

Previous investigators of the polymerization of olefin gases have reported very poor results as regards the V. I. of the products. For example, Sullivan (Industrial and Engineering Chemistry, Vol. 23, page 604, 1931,) reports the oils obtained by polymerization of ethylene to be —150 V. I. Similarly Nash (J. Inst. Pet. Tech. Vol. 16, page 838, 1930) reports viscosity-temperature data for lubricating oils produced by this method, which in our present terms of viscosity index correspond respectively to —5 V. I. and —47 V. I. Furthermore, Nash states that "the viscosities of these oils fall off more rapidly with rise in temperature than is the case with commercial lubricating oils of similar viscosity." Obviously, all of these products are much worse than even low grade oils from natural sources.

We have discovered that by suitable adjustment and careful regulation of conditions of time, temperature and pressure, and by the avoidance of the presence of active catalytic substances, we can obtain oils having higher V. I. than naturally occurring oils from any source instead of oils which are worse than most naturally occurring oils from this standpoint. The following table shows the character of the product which we obtain at 3,000 pounds pressure and at the temperatures shown, using a regulated time of contact.

Table I

Temperature °F.	Viscosity at 210° F. Saybolt (Univ.) secs.	Dean & Davis Viscosity Index
650	79	100
700	79	108
850	57*	11
950	41*	—60

* Overhead distillates, this being necessary on account of some tar formation in these runs.

It will be seen that the V. I. is at a maximum in the range 650–750° F. and falls off sharply above that point.

Previous workers, using uncontrolled or poorly controlled temperature and variable pressure conditions and operating in batchwise fashion, have reported that very long times of contact are necessary at temperatures of 750° F. in order to achieve conversion of ethylene to liquid products. Nash (supra) for example, reports that 7 hours or 420 minutes is necessary, while Ipatiev (Berichte Deut. Chem. Ges. Vol. 44, page 2978, 1911) found that 240 minutes was required. The use of such excessive times of contact apparently leads to undesired side reactions or reconversions. By careful control of our operating conditions and by operating within a limited range of temperatures and pressures in a continuous system, as elsewhere described herein, we find that entirely different results from those previously reported are obtained. Operation in a continuous system is also necessary to obtain the uniform conditions necessary to our process.

The variation in results with changes in the various operating conditions of this process is shown in the following tables.

Polymerizing ethylene in the absence of a catalyst at 3000 lbs./sq. in. pressure and 650° F. for various times of contact, the results are as follows: (In these tables the term "percent bottoms" refers to the percent of material in the product boiling above the gasoline boiling range,

which is indicative of the content of light and heavy lubricating oils.)

Table II

Time (minutes)	Percent conversion	Percent bottoms
15	7.5	66
30	19.5	73
57	31.5	73

Operating at 3000 pounds pressure and 700° F. the results are as follows:

Table III

Time (minutes)	Percent conversion	Percent bottoms
7	19.5	72
26	43.1	73
85	75.0	60

Operating at 3000 pounds pressure and 750° F. the results are as follows:

Table IV

Time (minutes)	Percent conversion	Percent bottoms
7	46.4	60
20	73.0	56
79	75.7	46

It will be seen that with increasing time of contact for each of these temperatures the percent conversion increases, but that (particularly at the higher temperatures) the lubricating oil content of the product tends to fall off. It will further be seen that the percent conversion for a given time of contact tends to increase rapidly with the temperature, but as shown by Table I the maximum temperature is sharply limited by the quality of the product.

As a result of these various facts, we find it necessary to operate in the temperature range of 650–750° at 3000 pounds per square inch pressure and preferably in the range of 675–725°, using a time of contact of 5–100 minutes, if high quality lubricating oils are to be obtained in good yields. In general, at the lower temperature of our preferred range, we use the longer time of contact, and vice versa. Ordinarily we prefer to operate under such conditions of time-temperature-pressure as to give between 30%–75% and preferably 40%–60% conversion of olefins to total liquids per pass since this gives the maximum yield of the desired high-quality products (on account of the fact that longer time and higher conversions cause degradation of the product first produced). The time of contact necessary for the 30–75% conversion at 3000 pounds pressures is about 60–100 minutes at 650° F., 20–70 minutes at 700° F., and 5–20 minutes at 750° F. For the preferred conversion range of 40–60% the time of contact will be approximately 90 minutes at 650° F., approximately 30 minutes at 700° F., and approximately 10 minutes at 750° F. In other words at a temperature of "t" (°F.) within the temperature range of 650–750° F. and at 3000 lbs. pressure the optimum time of contact (T) minutes may be expressed by the approximate formula

$$50 \log T = 50 + (750 - t) \log 3$$

this value applying to relatively pure olefin gases within limits of ±10%.

To show the great effect of pressure on the results, the data of the following Table V may be noted, showing experiments carried out at 700° F. with 7 minutes time of contact.

Table V

Pressure lbs./sq. in.	Percent conversion	Percent bottoms
2000	4.8	48
3000	19.5	72

It is necessary to use pressures of at least 2000 pounds and preferably of at least 3000 pounds to obtain good yields of high quality lubricating oils, and we find that still higher pressures give still further improved results. Pressures of 5000–10,000 pounds per square inch may be used advantageously. With higher pressures, low temperatures may be employed. For example, at pressures in the range of 3000–5000 pounds, we may use temperatures of 600–700° F., while at pressures of 10,000 pounds, we may use temperatures as low as 500° F. At higher pressures considerably shorter times of contact may be used at a given temperature. By doubling the pressure, similar yields of liquid products may be obtained in from 50–75% of the time of contact at the lower pressure.

The apparatus for carrying out our improved process and the actual operation thereof is very simple and the drawing attached hereto and which forms part of this specification represents a diagrammatic elevational view of suitable apparatus for our process.

Referring to the drawing gases containing at least 50% by volume of gaseous olefins are introduced through line 10 and are compressed by compressor 11 to pressures of 2500–10,000 pounds per sq. in. following which they are passed through heater 12, wherein they are heated to temperatures of 500–750° F. prior to their introduction into unheated reaction drum 13. From drum 13 the products pass through line 14 to cooler 15, following which they pass through valve 15a into separator 16, which ordinarily is operated at as high pressure as possible consistent with proper phase separation of liquids and gases (this is usually not over 2000 pounds per square inch) and from which gases may be vented through offtake 17 or recycled through line 18 by booster 19 to the inlet of heater 12. Liquids and dissolved gases are withdrawn from separator 16 through offtake 20, the pressure reduced by valve 21 and the final liquid products separated from dissolved gases in separator 22. Gases removed in 22 may be eliminated from the system through line 23 or may be recycled through line 24 to the gas supply line 10 leading to compressor 11. Liquid products from separator 22 may be reheated and fractionated in tower 25 (which is provided with heating and fractionating means not shown) and all or a part of the light and intermediate liquid products which are removed as vapor from bubble tower 25, condensed in cooler 26 may be drawn off thru 26a or may be recycled by pump 27 thru line 27a to the inlet of heater 12, whereby the ultimate yield of higher boiling liquid products suitable for lubricating oils may be increased. Desired heavy lubricating stocks are drawn from tower 25 thru offtake 28. The final heavy lubricating stocks

may be redistilled to eliminate small proportions of tarry or asphaltic constituents, and/or may be treated with acid, clay, or other conventional lubricant refining methods. It will also be understood that separators 16 and 22 may be supplied with bubble plates, baffles, heating and cooling coils and other conventional means for improving separation therein.

The foregoing being a full and complete description of our invention,

We claim:

1. A process for the production of lubricating oils having a viscosity index of at least 100 by a polymerization process wherein the lubricating oil produced by the process comprises a substantial proportion of the total normally liquid products, which comprises subjecting gaseous olefins in the absence of active catalysts to a temperature "*t*" (° F.) in the range 650–750° F. while under a pressure of approximately 3000 pounds per square inch for a time "T" (minutes) substantially as defined by the relationship

$$50 \log T = 50 + (750 - t) \log 3$$

2. A process for the production of high viscosity index lubricating oils which comprises subjecting normally gaseous olefins in the absence of active catalysts to a temperature of about 675–725° F. under a pressure of about 3000 pounds per square inch for a time as defined by the following formula:

$$50 \log T = 50 + (750 - t) \log 3$$

where T is time in minutes and *t* is temperature in degrees F.

3. A process for the production of high viscosity index lubricating oils which comprises subjecting normally gaseous olefins in the absence of active catalysts to a temperature of about 500–750° F. under a pressure of about 2500–10,000 pounds per sq. in. for a time within about ±10% of that defined by the following formula:

$$50 \log T = 50 + (750 - t) \log 3$$

where T is time in minutes and *t* is temperature in degrees F.

4. A process as defined in claim 3 which also comprises fractionating liquid products produced by the polymerization step into heavy liquids and light liquids, recycling light liquids and treating said light liquids in the reaction system in admixture with normally gaseous olefins as defined in claim 3.

5. A process as defined in claim 1 which also comprises fractionating liquid products produced by the polymerization step into heavy liquids and light liquids, recycling light liquids and treating said light liquids in the reaction system in admixture with normally gaseous olefins as defined in claim 1.

6. A process as defined in claim 2 which also comprises fractionating liquid products produced by the polymerization step into heavy liquids and light liquids, recycling light liquids and treating said light liquids in the reaction system in admixture with normally gaseous olefins as defined in claim 2.

7. A process for the production of high viscosity index lubricating oils which comprises subjecting normally gaseous olefins in the absence of active catalysts to a temperature within the range of 650–750° F. while under a pressure within the range of 2000–3000 lbs. per square inch for a time within about ±10% of that defined by the following formula:

$$50 \log T = 50 + (750 - t) \log 3$$

where T is time in minutes and *t* is temperature in degrees F.

8. A process for the production of high viscosity index lubricating oils which comprises subjecting a gas consisting mostly of ethylene in the absence of active catalysts to a temperature within the range of 650–750° F. under a pressure within the range of 2000–3000 lbs. per square inch for a time within about ±10% of that defined by the following formula:

$$50 \log T = 50 + (750 - t) \log 3$$

where T is time in minutes and *t* is temperature in degrees F.

9. In a process for the production of high viscosity index lubricating oils, the steps comprising subjecting normally gaseous hydrocarbons consisting mostly of ethylene, in the absence of active catalysts, to a temperature of from 500–750° F. under pressures of 2,500 to 10,000 pounds per square inch for a time within ±10% of that defined by the following formula:

$$50 \log T = 50 + (750 - t) \log 3$$

where T is time in minutes and *t* is temperature in degrees F.

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