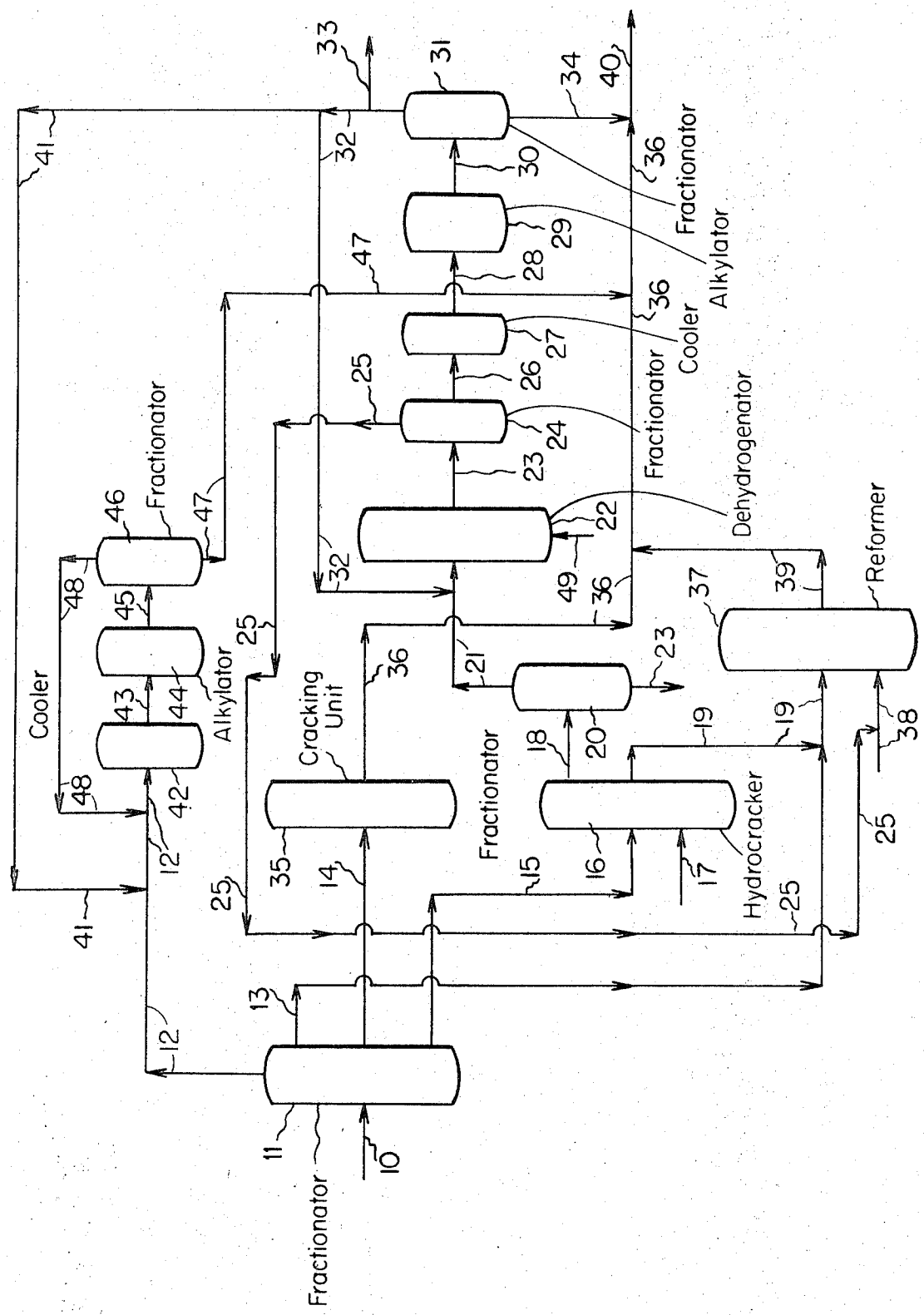
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GASOLINE MANUFACTURE

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GASOLINE MANUFACTURE

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U.S. Cl. 208—60 10 Claims

ABSTRACT OF THE DISCLOSURE

The production of high octane gasoline from a hydrocarbon charge stock is maximized by fractionating the same to obtain a gasoline fraction (a), a catalytic cracking charge stock (b), and hydrocracking charge stock (c). Stock (c) is hydrocracked to form gasoline fraction (d) and isobutane which is dehydrogenated selectively to form a mixture of isobutene and isobutane suitable as an alkylation charge. The mixture is alkylated to high octane gasoline components and recovered isobutane is recycled for selective dehydrogenation.

This invention has to do with the manufacture of gasoline and, more particularly, with maximizing the production of high octane gasoline from a hydrocarbon charge stock.

In recent years, considerable attention has been focused upon pollution of air by a variety of chemicals. Among the chemicals singled out for attention are lead compounds alleged to be expelled into the atmosphere from automobile, bus and truck exhausts. Legislation has been prepared with lower tetraethyllead (TEL) and tetramethyllead (TML) contents of gasolines, and with even an absence of such compounds, with a view toward reducing the possibility of lead compounds passing from vehicle, internal combustion engines into the atmosphere. Since lead alkyls, and particularly TEL increase the octane number of fuels, it follows that any reduction in lead alkyl content will have to be remedied by including other high octane components in gasolines. Thus, a demand is created for alkylate and reformate components.

Another attack has been directed at volatile components in gasolines. Legislation in preparation calls for reducing gasoline volatility. One result is that normal butane and isobutane would be omitted or the quantities now in use would be decreased markedly. The normal butane so made available could be isomerized to isobutane. As a consequence, a substantial quantity of isobutane would be available.

Apart from such developments in the petroleum field, the use of hydrocracking has increased substantially in recent years. One of the products obtained by hydrocracking of a variety of hydrocarbon stocks is isobutane. Thus, here again, a large quantity of isobutane has become available and, for economic refinery operation, it is obvious that some satisfactory use should be made of this hydrocarbon.

It is an object of the present invention, therefore, to provide a process for efficient utilization of isobutane and to maximize the production of high octane gasoline from a hydrocarbon charge stock.

As contemplated herein, "high octane gasolines" are those having an octane rating of at least about 90 (unleaded).

In accordance with the present invention, there is provided a process for producing high octane gasoline, which comprises:

(1) Contacting a hydrocarbon charge consisting essentially of isobutane with a dehydrogenating catalyst at a temperature from about 700° F. to a higher temperature at which substantially no cracking occurs, whereby a portion of the isobutane is dehydrogenated to isobutene, and

(2) Contacting the reaction product obtained in (1) with an alkylation catalyst under alkylating conditions to form said gasoline.

Another embodiment of the present invention is a process for producing high octane gasoline, which comprises:

(1) Contacting a gas oil with a hydrocracking catalyst under hydrocracking conditions whereby a reaction product containing isobutane and a gasoline fraction is formed;

(2) Separating said isobutane from the reaction product formed in (1);

(3) Contacting said isobutane with a dehydrogenating catalyst at a temperature from about 700° F. to a higher temperature at which substantially no cracking occurs, whereby a portion of the isobutane is dehydrogenated to isobutene, and

(4) Contacting the reaction product obtained in (3) with an alkylation catalyst under alkylation conditions to form said high octane gasoline.

A further embodiment of the invention involves a process for maximizing the production of a high octane gasoline from a hydrocarbon charge stock, which comprises:

(1) Fractionating said charge stock whereby a gasoline fraction (a), a catalytic cracking charge stock (b), and hydrocracking charge stock (c) are obtained,

(2) Contacting said stock (c) with a hydrocracking catalyst under hydrocracking conditions to form a gasoline fraction (d) and isobutane,

(3) Contacting said isobutane with a dehydrogenating catalyst at a temperature from about 700° F. to a higher temperature at which substantially no cracking occurs, whereby a portion of the isobutane is dehydrogenated to isobutane,

(4) Contacting the reaction producted obtained in (3) with an alkylation catalyst under alkylation conditions to form a high octane gasoline (e),

(5) Separating unreacted isobutane from the alkylation product obtained in (4) and recycling the unreacted isobutane to (3),

(6) Combining said gasoline fractions (a) and (d) and contacting the combined fractions with a reforming catalyst under reforming conditions to form a reformate gasoline, and

(7) Combining the reformate gasoline obtained in (6) and said high octane gasoline (e).

In order to facilitate description of the process contemplated herein, reference is now made to the accompanying drawing, which shows a typical flow diagram of a preferred arrangement for practicing the invention. The

flow diagram serves to illustrate the invention and, in no sense, to limit it.

In the flow diagram, a hydrocarbon charge stock is passed through line **10** to fractionator **11**. A gaseous stream containing isobutane is removed from fractionator **11** through line **12**, a gasoline fraction is removed through line **13**, a gas oil suitable as cracking stock is removed through line **14**, and a heavier gas oil suitable as hydrocracking stock is removed through line **15**.

The heavier gas oil in line **15** is passed into a hydrocracking unit **16** together with hydrogen from line **17**, wherein it is in contact with a suitable hydrocracking catalyst. Products obtained in unit **16** include an isobutane-rich fraction which is removed through line **18** and a gasoline fraction which is removed through line **19**.

The isobutane-rich fraction is passed through line **18** into fractionator **20** such that isobutane is removed therefrom as an overhead stream, which is passed through line **21** to dehydrogenator **22**. Normal butane present in the isobutane-rich fraction is removed from fractionator **20** through line **23** and is passed, for example, to an isomerization zone (not shown) for the production of additional isobutane.

In dehydrogenator **22**, isobutane is in contact with a suitable dehydrogenation catalyst under conditions selected to provide a relatively minor proportion of isobutene and to avoid any substantial cracking of the isobutane charge. The dehydrogenator product is passed from dehydrogenator **22** through line **23** into flash tower or fractionator **24** in order to remove hydrogen from the product. The hydrogen is removed through line **25** and can be employed as described below.

Dehydrogenator product free of hydrogen is cooled in tower **24** and further cooling can be accomplished, as desired, by passing this product through line **26** and cooler **27**. The cooled product is passed from tower **24** through line **28** into alkylator **29**, wehrein it is in contact with a suitable alkylation catalyst. An alkylation product containing a substantial proportion of isooctane is formed in alkylator **29**. The alkylation product is passed from **29** through line **30** to fractionator **31**.

Isobutane in the alkylation product is removed therefrom in fractionator **31** and is recycled through line **32** to line **21** and dehydrogenator **22**.

Purge line **33** is provided in conjunction with line **32** should it be necessary to remove contaiminants.

Alkylate predominating in isooctane is removed from fractionator **31** through line **34**. As explained below, the alkylate is blended or combined with one or more gasoline fractions.

The cracking stock in line **14** is charged to cracking unit **35** wherein it is in contact with a suitable cracking catalyst. One product formed in unit **35** is a gasoline fraction which is removed therefrom through line **36**. As shown, this gasoline fraction can be combined with the alkylate in line **34** and additional products as described below.

The straight run gasoline fraction in line **13** is combined with the hydrocracked gasoline in line **19** and is passed into reforming zone **37** wherein the combined gasoline fractions are in contact with a suitable reforming catalyst, preferably in the presence of hydrogen charged from line **38**. Hydrogen in line **25** can be routed from fractionator **26** to line **38** to supply part of the hydrogen requirements of reformer **37**. The reformate gasoline formed in zone **37** is removed thereform and is passed through line **39** to be combined with the gasoline in line **36**, and with the alkylate in line **34**. The combined products are removed through line **40**.

A gaseous overhead product from zone **11** contains isobutane and isobutene, which may be present in substantially equal proportions or one or the other may predominate dependent upon the hydrocarbon charge in line **10** and/or upon the operating conditions maintained in fractionator **11**. The gaseous product in line **12** is passed

with an additional quantity of isobutane recycled from line **32** to line **41** to cooler **42**, thence to line **43** and alkylator **44**. The alkylation product formed in alkylator **44** is passed through line **45** to fractionator **46**. Alkylate is removed from fractionator **46** through line **47** for combination with the gasoline fractions in line **36**. Isobutane in the alkylation product in fractionator **46** is passed through overhead line **48** for recycle to line **12**. As shown, a combined gasoline of high octane number can be removed from the system through line **40**.

Should hydrogen be charged to dehydrogenator **22**, it can be passed through line **49**.

By way of illustration, 100 gallons of a hydrocarbon charge comprising a Mid-Continent crude is fractionated in fractionator **11** into 40 gallons of straight run gasoline fraction in line **13**, 31 gallons of light gas oil in line **14**, and 28 gallons of heavier gas oil and residuum in line **15**. The straight run gasoline fraction has an octane number (unleaded) of about 38. The heavier gas oil is charged with hydrogen to hydrocracker **16**, the hydrogen being charged at a molar hydrogen to hydrocarbon charge ratio of about 2:1 to 80:1. Hydrocracking conditions employed are those conventionally used in the art, for example:

Temperature, ° F.	400–950
Pressure, p.s.i.g.	100–5000
Liquid hourly space velocity	0.1–10
H_2/hydrocarbon charge, molar	2–80

Similarly, conventional hydrocracking catalysts can be used, as those typified by cobalt molybdate on alumina, nickel-tungsten sulfide, and chromia on alumina.

Products obtained from the hydrocracking step include about 30 gallons of a gasoline fraction having an octane number (unleaded) of about 76, in line **19** and a quantity in line **18** corresponding to about 5.7 gallons of a C_4 fraction comprising about 4.1 gallons of isobutane and about 1.6 gallons of normal butane.

The C_4 fraction in line **18** is fractionated in fractionator **20**, the isobutane recovered therefrom being charged to dehydrogenator **22** wherein it is in contact with a conventional dehydrogenation catalyst such as an oxide or sulfide of any metal of Group VIA of Mendeleeff's Periodic Table, or mixture thereof. Typical of such catalysts are chromium sulfide, molybdenum sulfide and tungsten sulfide. Others include oxides and sulfides of Group VIII of said Periodic Table or mixture thereof, as illustrated by: the sulfides or iron, cobalt, nickel, palladium, platinum, rhodium, osmium and iridium. Still other catalysts include mixtures of the above oxides and sulfides of the metals of Group VIA and VIII of said Periodic Table, typified by mixtures of: nickel sulfide and tungsten sulfide; cobalt sulfide and molybdenum sulfide; and nickel sulfide and molybdenum sulfide. These metals can be deposited upon adsorbent carriers such as alumina, silica-alumina and silica-zirconia. The catalyst should have substantially no cracking activity and operating conditions are selected to avoid cracking of the C_4 charge. Generally, less than about 1 percent by volume of the charge is cracked when in contact with such catalysts.

Operating conditions for dehydrogenator **22** are selective such that the product will contain isobutane and isobutene in a molar ratio suitable for an alkylation charge, as from about 3:1 to about 15:1 and preferably 7:1 to 10:1. Expressed in another manner, approximate ratios of 3:1 to 15:1 will correspond to approximate isobutene contents of 5–40 percent by volume, and preferred approximate ratios of 7:1 to 10:1 will correspond to isobutene contents of 10–25 percent by volume. When hydrogen is not charged to zone **20**, the temperature is maintained between about 700° F. and about 970° F. preferably 750–900° F. When hydrogen is also charged to zone **20**, particularly to extend catalyst life, the temperature will

range from about 870° F. to about 1050° F., preferably 920–1000° F. When hydrogen is charged, it is charged at a molar hydrogen to hydrocarbon charge ratio of about 2:1 to 10:1. Pressure can be atmospheric, subatmospheric or above atmospheric. In general, conversion of i-C_4 to isobutene increases with lower pressures and decreases with higher pressures.

The dehydrogenation product obtained in dehydrogenator **22** contains a balance of isobutane and isobutene, as explained above, and is suitable for alkylation without modification. It is removed from dehydrogenator **22** through line **23** and is passed to fractionator **24** for removal of hydrogen therefrom via line **25**. The hydrogen-free dehydrogenation product in line **26** is cooled in cooler **27** and is passed through line **28** into alkylator **29**. The cooled product is in contact in alkylator **29** with a conventional alkylation catalyst such as hydrogen fluoride, sulfuric acid and aluminum chloride. Conventional alkylation conditions are employed such as those for HF alkylation, namely: 0–150° F.; pressures at least sufficiently high to keep the C_4 hydrocarbons and HF in the liquid phase; HF:hydrocarbon of at least 1:1 reaction time, 1–60 minutes; and HF titratable acidity of 70–90 percent by weight.

The alkylation product is passed from alkylator **29** through line **30** to fractionator **31**. Approximately 1.2 gallons of alkylate, predominately isooctane, are recovered through line **34** and approximately 2.9 gallons of isobutane are removed from fractionator **31** through line **32**. The isobutane in line **32** is recycled to line **21** to extinction in dehydrogenator **22** thereby providing about 4 gallons of alkylate. A portion of the isobutane in line **32** can also be passed through line **41** to alkylator **44** to provide a part of the isobutane required therein.

Returning to fractionator **11**, the quantity (31 gallons) of light gas oil in line **14** is passed to cracking unit **35** wherein it is cracked in the presence of a conventional cracking catalyst under customary cracking conditions. Fixed bed (e.g. Houdry), TCC and fluid processes are typical of those which can be employed. Since the catalysts and operating conditions are well-known in the art, reference is made to the literature and patents which are available. As shown in the flow diagram, a gasoline fraction comprising about 16 gallons and having an octane number (unleaded) of about 89.3, is removed from unit **35** through line **36** and is combined with the reformate in line **39**.

The reformate in line **39** is obtained by combining the 40 gallons of straight run gasoline fraction (octane number, 38) in line **13** with the 30 gallons of hydrocracked gasolin (octane number, 76) in line **19**, and charging the combined gasolines to reformer **37**. In **37**, they are in contact with a typical reforming catalyst under customary reforming conditions. Suitable catalysts are platinum group metals with or without a halogen, particularly chlorine. Reforming conditions are typified by and include: 500–1200 p.s.i.g., 900–980° F., and liquid hourly space velocity of 0.5–3. As shown, hydrogen can be charged from line **38** to reformer **37**. The reformate product comprises about 55 gallons and has an octane number of about 89.7. It is removed from reformer **37** through line **39** for combination with gasoline in line **36** and alkylate in line **34**.

In accordance with this illustration, there is obtained aproximately 75 gallons of combined gasoline product in line **40** from the original 10 gallons of hydrocarbon charge from line **10**. The gasoline product in line **40** has an octane rating of about 90.2, in contrast to an octane rating of about 89.6 for the 71 gallons of gasolines combined from only lines **36** and **39**.

It is to be understood that hydrocarbon charge stocks passed from line **10** to fractionator **11** can be crudes of paraffinic, naphthenic and other character, and can be topped or desalted crudes.

I claim:

1. In a process for producing high octane gasoline components wherein isobutane is dehydrogenated catalytically to form isobutene and the isobutene and isobutane are alkylated catalytically to form said gasoline components, the improvement which comprises:

(1) contacting a hydrocarbon charge consisting essentially of isobutane with a dehydrogenating catalyst at a temperature from about 700° F. to a higher temperature at which substantially no cracking occurs, whereby a portion of the isobutane is dehydrogenated to isobutene and the resulting iso-C_4 dehydrogenation reaction product contains isobutane and isobutene in a molar ratio of from about 3:1 to about 15:1 of isobutane to isobutene, and

(2) contacting substantially all of the i-C_4 reaction product obtained in (1) consisting essentially of isobutane and isobutene with an alkylation catalyst under alkylating conditions to form said gasoline components.

2. Process of claim **1** wherein unreacted isobutane is recovered from the alkylation product of (2) and is recycled to (1).

3. Process as defined by claim **1**, wherein the temperature in (1) is from about 750° F. to about 900° F.

4. Process as defined by claim **1**, wherein the isobutane is so contacted in (1) in the presence of hydrogen at a temperature of from about 870° F. to about 1050° F.

5. Process as defined by claim **4**, wherein the temperature is from about 920° F. to about 1000° F.

6. In a process for producing high octane gasoline wherein a gas oil is contacted with a hydrocracking catalyst under hydrocracking conditions whereby a reaction product containing isobutane and a gasoline fraction is formed, wherein said isobutane is separated from said reaction product, and wherein said isobutane is dehydrogenated catalytically to form isobutane and the isobutene and isobutane are alkylated to form high octane gasoline components, the improvement which comprises:

(1) contacting said isobutane with a dehydrogenating catalyst at a temperature from about 700° F. to a higher temperature at which substantially no cracking occurs, whereby a portion of the isobutane is dehydrogenated to isobutene and the resulting iso-C_4 dehydrogenation reaction product contains isobutane and isobutene in a molar ratio of from about 3:1 to about 15:1 of isobutane to isobutene, and

(2) contacting substantially all of the i-C_4 reaction product obtained in (1) consisting essentially of isobutane and isobutene with an alkylation catalyst under alkylation conditions to form high octane gasoline components.

7. Process of claim **6** wherein unreacted isobutane is recovered from the alkylation product of (2) and is recycled to (1).

8. Process of claim **6** wherein said gasoline fraction is recovered and is contacted with a reforming catalyst under reforming conditions to form a reformate gasoline.

9. Process of claim **8** wherein said reformate and said high octane gasoline are combined.

10. In a process for maximizing the production of high octane gasoline from a hydrocarbon charge stock, wherein said charge stock is fractionated to provide a gasoline fraction (a), a catalytic cracking charge stock (b) and hydrocracking charge stock (c), wherein stock (c) is contacted with a hydrocracking catalyst under hydrocracking conditions to form a gasoline fraction (d) and isobutane, and wherein said isobutane is dehydrogenated catalytically to form isobutane and the isobutene and isobutane are alkylated to form high octane gasoline components, the improvement which comprises:

(1) contacting said isobutane with a hydrogenating catalyst at a temperature from about 700° F. to a higher temperature at which substantially no cracking occurs, whereby a portion of the isobutane is

dehydrogenated to isobutene and the resulting iso-C_4 dehydrogenation reaction product contains isobutane and isobutene in a molar ratio of from about 3:1 to about 15:1 of isobutane to isobutene,

(2) contacting substantially all of the i-C_4 reaction product obtained in (1) consisting essentially of isobutane and isobutene with an alkylation catalyst under alkylation conditions to form high octane gasoline components (e),

(3) separating unreacted isobutane from the alkylation product obtained in (2) and recycling the unreacted isobutane to (1),

(4) combining said gasoline fractions (a) and (d) and contacting the combined fractions with a reforming catalyst under reforming conditions to form a reformate gasoline, and

(5) combining the reformate gasoline obtained in (4) and said high octane gasoline components (e).

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208—68, 79, 112; 260—683.3, 683.43

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,530,060 Dated September 22, 1970

Inventor(s) ROBERT D. OFFENHAUER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 37, "wehrein" should be --wherein--.
Column 3, line 66, "thereform" should be --therefrom--.
Column 5, line 51, "gasolin" should be --gasoline--.
Column 5, line 67, "10 gallons" should be --100 gallons--.

SIGNED AND
SEALED
DEC 8 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents