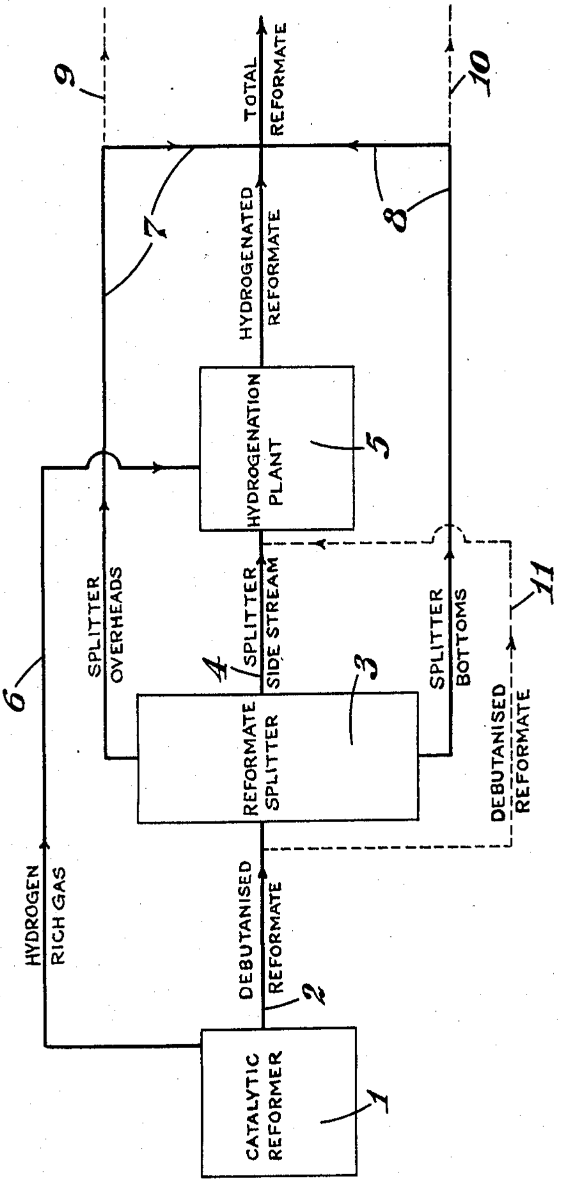
Jan. 12, 1960 K. S. CUDDINGTON ET AL 2,921,016

CATALYTIC REFORMING OF PETROLEUM HYDROCARBONS

Filed Oct. 31, 1956



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United States Patent Office

2,921,016

Patented Jan. 12, 1960

2,921,016

CATALYTIC REFORMING OF PETROLEUM HYDROCARBONS

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Application October 31, 1956, Serial No. 619,511

Claims priority, application Great Britain November 11, 1955

8 Claims. (Cl. 208—95)

This invention relates to the catalytic reforming of petroleum hydrocarbons in order to increase their suitability for use as motor fuels. More particularly the invention relates to improvements in the so-called Platforming process wherein hydrocarbons are contacted in the presence of hydrogen with a platinum-containing catalyst.

Platforming is capable of producing a considerable increase in the octane number of straight-run petroleum feedstocks in the motor gasoline boiling range, but it has recently been noted that the octane number of the Platformate falls off rapidly on exposure to light and air, and that this effect cannot be prevented by the use of oxidation inhibitors. A similar loss of octane number is not shown by catalytically cracked or steam cracked gasoline, so that the component or components causing the octane number loss appear to be formed by the reforming operation itself. The extent of the loss in the octane number in respect of a typical Platformate is illustrated in the following Table 1, and compared with the loss for samples of catalytically cracked and steam cracked gasolines.

Table 1

Material	Time of Exposure, Days	Octane Number—Research		
		Unexposed	Exposed	Loss
Platformate No. 1	1	87.8	82.8	5.0
Platformate No. 2	2	89.5	83.8	5.7
Platformate No. 3	2	93.2	88.5	4.7
Catalytically cracked spirit	6	94.5	94.0	0.5
Steam cracked gasoline	1	94.0	93.9	0.1

It has now been discovered that such loss of octane number may be reduced or prevented by subjecting the Platformate to mild hydrogenation.

According to the present invention therefore, loss of octane number due to the exposure of a catalytic reformate, in particular a Platformate, to light and air is reduced or prevented by subjecting the reformate to a mild hydrogenation.

In carrying the invention into effect according to a preferred embodiment, the reformate is contacted with hydrogen in the presence of a hydrogenation catalyst under the following conditions:

Pressure	p.s.i.g.	0–500
Temperature	° F.	300–500
Space velocity	v./v./hr.	0.1–1.0
Hydrogen or hydrogen-rich gas rate	s.c.f./b.	2000–4000

The preferred catalyst is a sulphur resistant hydrogenation catalyst particularly one or more of the sulphides of a group VI or group VIII metal, for example a mixture of nickel and tungsten sulphides.

In a specific example, a sample of debutanised Platformate having a research octane number of 87.1 was

exposed to air and light for 24 hours, after which time the research octane number had decreased to 81.5.

A second sample of the debutanised Platformate was hydrogenated under the following conditions:

Catalyst	Nickel/tungsten sulphides.
Reactor pressure	250 p.s.i.g.
Reactor temperature	435° F.
Space velocity	0.25 v./v./hr.
Recycle hydrogen rate	3000 s.c.f./b.

After hydrogenation, the Platformate had a research octane number of 86.5 which after 96 hours' exposure to air and light had only decreased to 86.1.

It has furthermore been discovered that the component or components responsible for the light-catalysed octane number loss are contained in the fraction of the Platformate boiling between 100° and 138° C., as illustrated in the following Table 2.

Table 2

Fraction of Platformate	Time of Exposure, Days	Octane Number—Research		
		Unexposed	Exposed	Loss
Total Platformate	2	89.5	83.8	5.7
IBP–138° C. (60% vol.)	1	72.2	68.1	4.1
IBP–100° C	1	70.7	70.5	0.2
100°–138° C	1	76.3	69.2	7.1
138° C.–End Point (40% vol.) (45% wt. residue).	3	IC_8+0.23[1] ml. TEL/USG.	IC_8+0.23[1] ml. TEL/USG.	Nil

[1] Approximately equivalent to 102.3 on the octane number scale.

According to a further method of carrying the method into effect therefore, the fraction of Platformate boiling between 100° and 138° C. is separated and subjected to mild hydrogenation as above described, the hydrogenated fraction being then blended back with the remaining portions of the Platformate.

The hydrogenation treatment in accordance with the invention may be carried out as an operation separate and distinct from the Platforming operation. If desired however, it may be carried out as part of a continuous process with the Platforming operation. In this case, the product from the Platforming operation is cooled and if necessary reduced in pressure before being passed to the hydrogenation reactor.

Examples of continuous process operation are illustrated in the accompanying flow diagram. Considering the embodiment illustrated by the solid flow lines, the products from a catalytic reformer **1** include liquid debutanised reformate and hydrogen-rich gas. The former is fed via line **2** to a reformate splitter **3** where it is fractionated into three streams, the middle of which contains substantially all the components giving rise to the light-catalysed octane number loss. This stream is passed via line **4** to a hydrogenation plant **5** supplied through line **6** with the hydrogen-rich gas from the catalytic reformer **1**. After hydrogenation, the stream is recombined with the splitter overheads and splitter bottoms which are fed via lines **7** and **8** respectively. The dotted continuations of the splitter overheads and the splitter bottoms lines (**9** and **10** respectively) illustrate a possible variant of the process in which the splitter streams are not recombined. The dotted line **11** by-passing the reformate splitter illustrates a further variant in which the total debutanised reformate is hydrogenated without previous splitting.

We claim:

1. A process for reducing loss of octane number due to exposure to light and air of a platinum reformate obtained by contacting a straight-run petroleum feedstock boiling in the gasoline range with a reforming catalyst

containing platinum, which comprises contacting the platinum reformate in the presence of hydrogen with a hydrogenation catalyst at a temperature of 300 to 500° F. and at a pressure of 0 to 500 p.s.i.g.

2. A process according to claim 1, wherein the space velocity is from 0.1 to 1 v./v./hr. of the liquid feedstock and the hydrogen or hydrogen-rich gas rate is from 2000 to 4000 s.c.f./b.

3. A process according to claim 1, wherein the catalyst comprises at least one sulphide of a metal selected from groups VI and VIII of the periodic table.

4. A process according to claim 1, wherein the catalyst comprises a mixture of nickel sulphide and tungsten sulphide.

5. A process for reducing loss of octane number due to exposure to light and air of a platinum reformate obtained by contacting a straight-run petroleum feedstock boiling in the gasoline range with a reforming catalyst containing platinum, which comprises separating from the platinum reformate a fraction having a boiling range of approximately 100 to 138° C., contacting said fraction in the presence of hydrogen with a hydrogenation catalyst at a temperature of 300° to 500° F. and at a pressure of 0 to 500 p.s.i.g., and adding the hydrogenated fraction to the remainder of the reformate.

6. A process according to claim 5, wherein the space velocity is from 0.1 to 1 v./v./hr. of the liquid feedstock and the hydrogen or hydrogen-rich gas rate is from 2000 to 4000 s.c.f./b.

7. A process according to claim 5, wherein the catalyst comprises at least one sulphide of a metal selected from groups VI and VIII of the periodic table.

8. A process according to claim 5, wherein the catalyst consists of a mixture of nickel sulphide and tungsten sulphide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,345,575	Burk et al.	Apr. 4, 1944
2,425,506	Bethea	Aug. 12, 1947
2,534,025	Howes et al.	Dec. 12, 1950
2,731,506	Love et al.	Jan. 17, 1956
2,740,751	Haensel et al.	Apr. 3, 1956