

Sept. 16, 1958

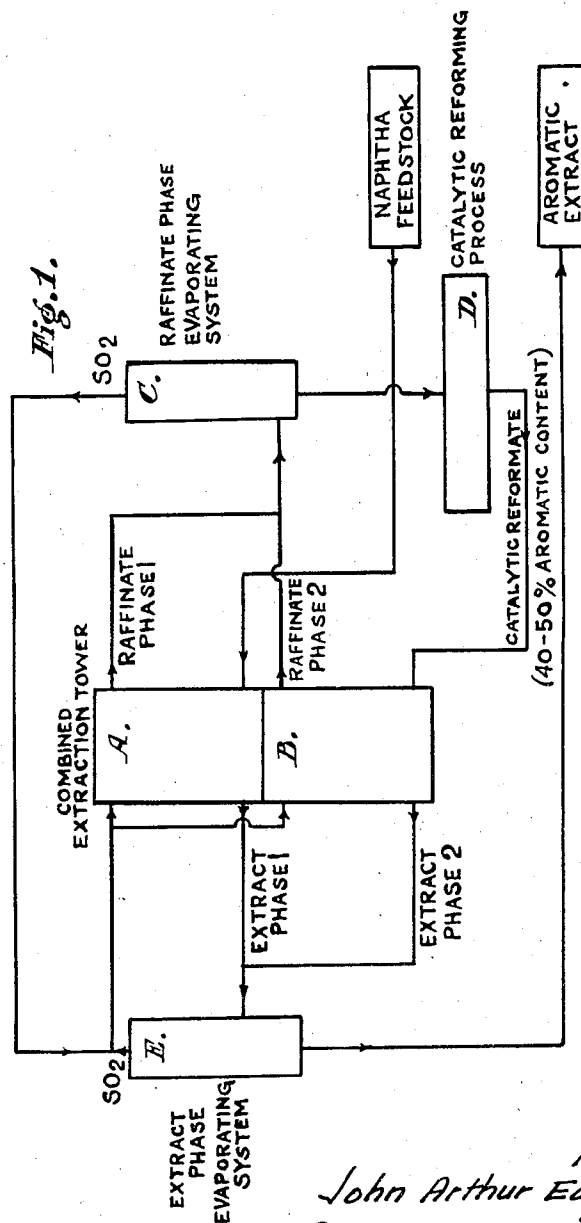
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CATALYTIC REFORMING OF PETROLEUM HYDROCARBONS

Filed Sept. 11, 1956

2 Sheets-Sheet 1



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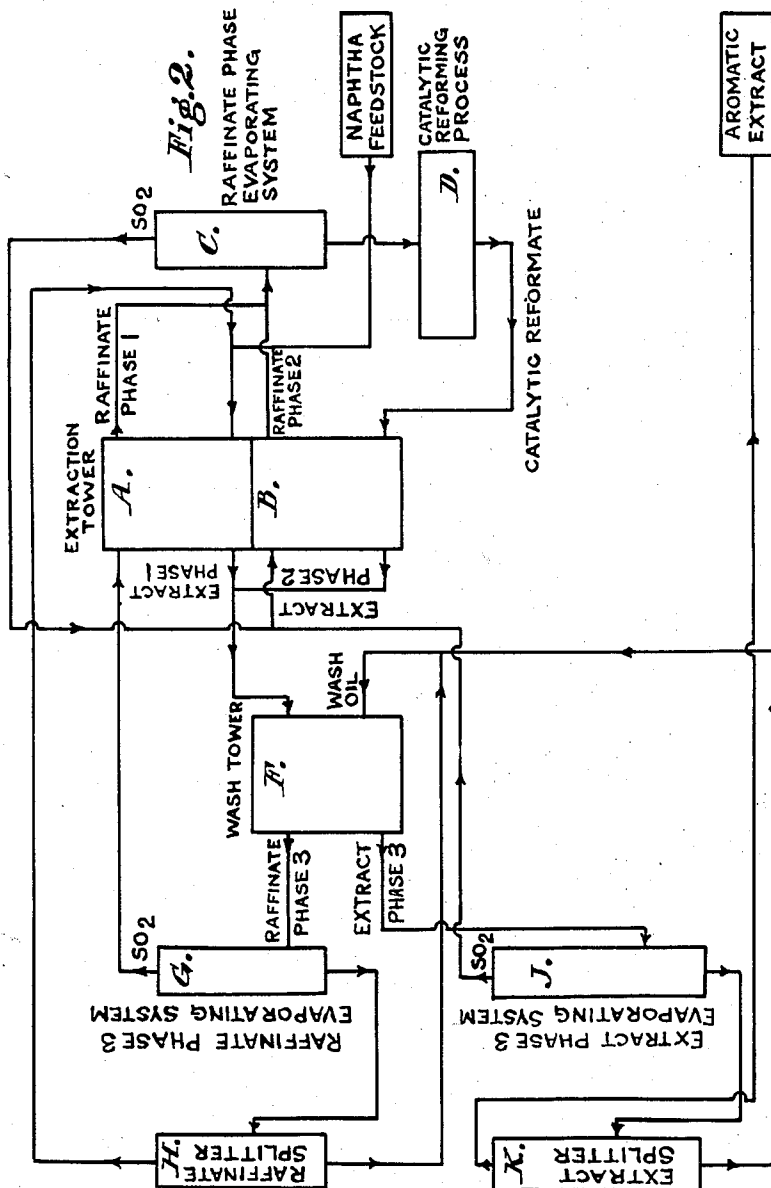
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CATALYTIC REFORMING OF PETROLEUM  
HYDROCARBONS

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Application September 11, 1956, Serial No. 609,146

Claims priority, application Great Britain  
September 23, 1955

6 Claims. (Cl. 196—50)

This invention relates to the catalytic reforming process which, as applied to petroleum hydrocarbons, consists in contacting the hydrocarbons at elevated temperature and pressure with a catalyst for the various chemical reactions which contribute to the production of aromatics whereby a product of increased aromatic content as compared with the feedstock is obtained.

The catalytic reforming process is particularly useful in the petroleum industry for treating naphtha fractions of low aromatic content and low octane number for the production of naphthas having increased aromatic content and higher octane number and therefore more suitable for use as motor gasolines. One such process which has been developed is the Platforming process in which a catalyst is used comprising a small amount of platinum, and sometimes a halogen, supported on an alumina base. In order to obtain a product of still higher octane number, it has recently been proposed to subject the initial reformate to solvent extraction to produce an extract rich in aromatics, the raffinate being returned to the reforming zone.

The present invention relates to a process of this latter kind and has among its objects to obtain a product having an aromatic content of 70–80%.

The process according to the present invention comprises contacting a catalytic reformer feedstock with liquid sulphur dioxide in conventional manner for the production of an aromatic extract and a raffinate, passing the raffinate to a catalytic reforming zone for the production of aromatics, contacting the product from the catalytic reforming zone with liquid sulphur dioxide in conventional manner for the production of an aromatic extract of the same aromatic content as the aromatic extract previously referred to, and a raffinate, and passing the raffinate to the catalytic reforming zone together with the raffinate previously referred to.

Extraction of aromatics from the naphtha feedstock is advantageous for two reasons: (a) an increased quantity of aromatics can be formed by increased dehydrocyclization of paraffins, (b) there is a reduction in quantity of unreactive compounds passing through the catalytic reforming process.

Extraction of aromatics from the catalytic reformate is a more effective method of obtaining a final product of the required aromatic content than is the operation of the catalytic reforming process at higher severity which would result in rapid deactivation of the catalyst.

The production of aromatic extracts of the same aromatic content may be accomplished by operating at the same temperature but with different solvent to oil ratios. This method of operation has the following advantages:

(a) The two extraction towers can be made as one column with two compartments.

(b) Only one system of raffinate phase evaporators and one system of extract phase evaporators are required since the relevant phases are combined.

A product of still greater aromatic content may be obtained according to a further feature of the invention

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by contacting countercurrently the aromatic extracts referred to above in solution in liquid sulphur dioxide with a non-aromatic hydrocarbon cut having a different boiling range from the extracts, whereby some of the non-aromatics present in the extracts are replaced by non-aromatics of different boiling range which may subsequently be removed by distillation, yielding a product of still greater aromatic content of up to 95%. Operation in this manner enables a highly aromatic extract to be produced economically. Production of such an extract by a conventional solvent extraction process would entail the use of a very low extraction temperature, about  $-70^{\circ}$  F., which would present problems in the materials of construction and would also be expensive. Furthermore, the washing operation may be conveniently carried out at the same temperature as the solvent extraction stages referred to, so that all three operations can be carried out in a single column having three compartments.

Two methods of carrying the invention into effect will now be described with reference to Figures 1 and 2 respectively of the accompanying drawings. Referring first to Figure 1, the feedstock, for example a naphtha boiling in the range  $90^{\circ}$  to  $190^{\circ}$  C. and containing 12 to 20% aromatics, is contacted countercurrently in a conventional multistage solvent extraction tower A at a temperature in the range  $-30^{\circ}$  to  $+20^{\circ}$  F. with liquid sulphur dioxide in the proportion of 50 to 150 volumes of sulphur dioxide per 100 volumes of naphtha. The solvent ratio is adjusted to give an extract containing the required concentration of aromatics. The products from this operation are raffinate phase 1 and extract phase 1.

Raffinate phase 1 is combined with raffinate phase 2 (as described below) and is passed to a raffinate phase evaporating system C where sulphur dioxide is removed from the substantially aromatic-free naphtha by distillation. The sulphur dioxide is recycled to the extraction tower.

The aromatic-free naphtha is passed to a catalytic reforming process D in which a product containing about 40 to 50% aromatics is made.

The stabilized reformate is passed to a second conventional multistage solvent extraction tower B in which it is contacted countercurrently at a temperature in the range  $-30^{\circ}$  to  $+20^{\circ}$  F. with liquid sulphur dioxide in the proportion of 200 to 400 volumes of sulphur dioxide per 100 volumes of reformate. The solvent ratio is adjusted to give an extract containing the required concentration of aromatics which is the same concentration as that obtained from the first extraction operation. The products from this operation are raffinate phase 2 and extract phase 2.

Raffinate phase 2 is combined with raffinate phase 1 (as described above) before passing to the raffinate phase evaporators C in which sulphur dioxide is removed from the substantially aromatic-free naphtha which is recycled (with the dearomatized naphtha feedstock) to the reforming process.

Extract phase 2 is combined with extract phase 1 before passing to the extract phase evaporating system E where sulphur dioxide is removed from the hydrocarbon component and recycled to the extraction towers. The hydrocarbon component is the desired product containing 70% to 80% aromatics.

Referring now to Figure 2, the operation is the same as described with reference to Figure 1 up to the point where extract phases 1 and 2 are combined. The combined stream is then passed to a wash tower F where it is contacted countercurrently with a non-aromatic hydrocarbon cut which boils outside the range of the extracted hydrocarbon, a de-aromatized heavy kerosine but being preferred. The ratio of the volume of wash

oil to the volume of hydrocarbons in the combined extract phase is in the range 0.25 to 1.5 to 1. The washing operation is carried out at the same temperature as the solvent extraction stage. The product from this operation are raffinate phase 3 and extract phase 3.

Raffinate phase 3 is passed to an evaporating system G where sulphur dioxide is distilled off and recycled to the extraction towers A and B, while the hydrocarbon part of the raffinate phase is fed to a raffinate splitter H. The splitter will give material in the naphtha boiling range as an overhead product which is recycled to the extraction tower A, and kerosine as a bottoms product which is recycled to the wash tower F.

Extract phase 3 is passed to an evaporating system J where sulphur dioxide is distilled off and recycled to extraction towers A and B, while the hydrocarbon part of the extract phase is fed to an extract splitter K. The splitter will give as an overhead product the required product containing 95% aromatics, and kerosine as a bottoms product which is recycled to the wash tower F.

I claim:

1. A process for the catalytic reforming of a petroleum feedstock, which comprises contacting the feedstock with liquid sulphur dioxide for the production of an aromatic extract and a raffinate, passing the raffinate to a catalytic reforming zone for the production of aromatics, contacting the product from the catalytic reforming zone with liquid sulphur dioxide for the production of an aromatic extract and a raffinate, the contacting of the feedstock and the contacting of the product of the catalytic reforming zone with liquid sulphur dioxide being carried out at the same temperature but with different solvent to oil ratios to give aromatic extracts of the same aromatic content, and passing the raffinate to the catalytic reforming zone together with the raffinate previously referred to.

2. A process according to claim 1, wherein the feedstock consists of a naphtha fraction.

3. A process according to claim 2, wherein the naphtha fraction is contacted at a temperature in the range  $-30^{\circ}$  to  $+20^{\circ}$  F. with liquid sulphur dioxide in the proportion of 50 to 150 volumes of sulphur dioxide per 100 volumes of naphtha.

4. A process according to claim 2, wherein the product of the catalytic reforming zone is contacted at a temperature in the range  $-30^{\circ}$  to  $+20^{\circ}$  F. with liquid sulphur dioxide in the proportion of 200 to 400 volumes of sulphur dioxide per 100 volumes of product.

5. A process for the catalytic reforming of a petroleum feedstock, which comprises contacting the feedstock with liquid sulphur dioxide for the production of an aromatic extract and a raffinate, passing the raffinate to a catalytic reforming zone for the production of aromatics, contacting the product from the catalytic reforming zone with liquid sulphur dioxide for the production of an aromatic extract of the same aromatic content as the aromatic extract previously referred to, passing the raffinate to the catalytic reforming zone together with the raffinate previously referred to, combining said aromatic extracts, contacting the combined extracts, in solution in liquid sulphur dioxide, countercurrently with a dearomatized heavy kerosine fraction, the ratio of said kerosine fraction to the hydrocarbons in the combined extracts being in the range of 0.25 to 1.5:1 by volume, and distilling the extracts after being thus contacted for the recovery of a product of increased aromatic content.

6. A process according to claim 5, wherein said contacting with a dearomatized heavy kerosine fraction is carried out at the same temperature as the solvent extraction stages.

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**UNITED STATES PATENT OFFICE**  
**CERTIFICATION OF CORRECTION**

Patent No. 2,852,442

September 16, 1958

John Arthur Edgar Moy

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 34, before "raffinate" insert -- last mentioned --.

Signed and sealed this 13th day of June 1961.

(SEAL)

Attest:

**ERNEST W. SWIDER**

Attesting Officer

**DAVID L. LADD**

Commissioner of Patents