# United States Patent [19]

# Jones

### [54] PRODUCTION OF GASEOUS OLEFINS FROM PETROLEUM RESIDUE FEEDSTOCKS

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- 208/89

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3,720,729	3/1973	Sze et al 208/57
3,781,195	12/1973	Davis et al 208/57

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# [11] 3,898,299 [45] Aug. 5, 1975

#### [57] ABSTRACT

Normally gaseous olefins are produced from an atmospheric petroleum residue feedstock by:

- a. contacting the feedstock in a hydrogenation zone with a hydrogenation catalyst, of which nickel/tungsten/silica/alumina and cobalt/molybdenum/alumina are most suitable, under conditions which effect hydrogenation of aromatic hydrocarbons. Typical conditions are a temperature in the range 50° to 500°C, a pressure in the range 50 to 500 psig, and an LHSV of 0.1 to 5.0 with a hydrogen feed rate of 5 to 10 times the molar feed rate of the feedstock.
- b. separating from the hydrogenated feedstock a gaseous phase containing hydrogen and a liquid phase containing hydrocarbons.
- c. recycling at least a portion of said gaseous phase containing hydrogen to said hydrogenation zone.
- d. separating the liquid phase from (c) into a distillate fraction having a boiling range below 650°C and a residue fraction having a higher boiling range, advantageously by vacuum distillation.
- e. subjecting the distillate fraction from (d) to thermal cracking in the presence of steam thereby converting at least a portion of the liquid phase to normally gaseous hydrocarbons and
- f. recovering the normally gaseous olefins from the pyrolysis zone effluent.

# **10 Claims, No Drawings**

#### PRODUCTION OF GASEOUS OLEFINS FROM PETROLEUM RESIDUE FEEDSTOCKS

The present invention relates to a process for the production of normally gaseous olefins from atmospheric 5 petroleum residue feedstocks.

In the operation of a typical oil-refinery crude oil is initially fed to a distillation unit where it is separated at atmospheric pressure into benzine (motor spirit), naphtha, kerosine and gas oil. The residue from the at- 10 mospheric distillation unit, hereinafter to be referred to as an atmospheric petroleum residue feedstock, is composed of fractions boiling under atmospheric pressure at a temperature greater than 300°C. This residue may either be used directly as fuel oil or as feedstock to a 15 ture and pressure. distillation unit operating at reduced pressure. The distillate from the distillation unit operating at reduced pressure, otherwise known as a vacuum distillate, may be used as catalytic cracker feedstock or used in lubricating oil manufacture whilst the residue, hereinafter to 20 be referred to as the vacuum residue, may be blended for use as fuel oil.

An alternative use for the vacuum distillate is described in Davis et al. U.S. Pat. No. 3,781,195, which describes a process for the production of olefins by hy-25 drogenating a petroleum distillate feedstock in the presence of a hydrogenation catalyst and hydrogen and thermally cracking the resulting hydrogenated product in the presence of steam. Whilst this process leads to a number of substantial advantages there are disadvantages when using high sulphur feedstock (e.g. from typical Middle East sources). Using these feedstocks a large quantity of vacuum residue is co-produced with the vacuum distillate. The vacuum residue contains higher sulphur levels than the initial petroleum residue 35 feedstock to the vacuum distillation unit and is more difficult to desulphurise than either the vacuum distillate or the petroleum residue feedstock. With increasing restrictions on fuel oil sulphur levels in many countries high sulphur vacuum residues will become increasingly difficult to dispose of and will consequently adversely effect the economics of the overall process. Further only a part of the atmospheric petroleum residue feedstock is utilised as hydrogenated petroleum distillate feedstock to the steam cracker, the remaining carbon in the vacuum residue being lost to olefins production.

It has now been discovered that the first of these disadvantages can be substantially overcome and the fraction of the atmospheric petroleum residue feedstock utilised as feedstock to the steam cracker increased by hydrogenating the atmospheric petroleum residue feedstock prior to distillation.

Thus according to the present invention there is provided a process for the production of normally gaseous olefins from an atmospheric petroleum residue feedstock which process comprises contacting the atmospheric petroleum residue feedstock in a hydrogenation zone with a hydrogenation catalyst and hydrogen under conditions which effect hydrogenation of aromatic hydrocarbons, separating from the resulting hydrogenated atmospheric petroleum residue feedstock a gaseous phase containing hydrogen and a liquid phase containing hydrocarbons, recycling at least a portion of said gaseous phase to said hydrogenation zone, separating said liquid phase into a distillate fraction and a residue fraction, subjecting said distillate fraction in the

presence of steam to thermal cracking in a pyrolysis zone under conditions effecting conversion of at least a portion of said liquid phase to normally gaseous olefins and thereafter recovering the normally gaseous olefins from the pyrolysis zone effluent.

Distillate fraction within the context of the present application means that fraction of the liquid phase containing hydrocarbons having a boiling range below 650°C at atmospheric pressure and residue fraction that fraction having a boiling range above that of the distillate fraction.

The term 'normally gaseous olefins' within the context of the present application is intended to mean olefins which exist in the form of gases at normal temperature and pressure.

The whole of the liquid phase containing hydrocarbons resulting from the hydrogenation of the atmospheric petroleum residue feedstock may, after separation of a gaseous phase containing hydrogen, be fed in 20 the presence of steam directly to the pyrolysis zone wherein unvapourised feedstock is removed as a residue fraction in a separation zone prior to entry of the vapourised distillate fraction into that region of the pyrolysis zone maintained under conditions which effect 25 thermal cracking. The temperature of the liquid phase containing hydrocarbons/steam mixture fed to the pyrolysis zone is preferably regulated to maximise the proportion of hydrocarbons in the distillate fraction without promoting incipient thermal cracking of the 30 mixture.

It is preferred however to separate the liquid phase containing hydrocarbons resulting from hydrogenation of the atmospheric petroleum residue fraction, after separation of a gaseous phase containing hydrogen, into a distillate fraction and a residue fraction by distillation under reduced pressure and feed only the vacuum distillate fraction in the presence of steam to the pyrolysis zone.

Thermal cracking within the context of this application is intended to include steam cracking but not catalytic cracking.

Hydrogenation of the petroleum residue feedstock not only achieves hydrogenation of aromatics thereby leading to a reduction in boiling point of the compounds involved and an increase in the proportion of the feedstock available for thermal cracking to gaseous olefins but also effects desulphurisation of the feedstock, leads to substantially increased yields of useful olefins for a given quantity of feedstock and results in a reduction of coke laydown in the cracking coil and of tar deposits in transfer lines and heat exchangers.

It is important to avoid excessive breakdown of the feedstock in a hydrocracking type of reaction. A limited amount of hydrocracking can be tolerated and may even give the benefit of producing a more mobile product but excessive hydrocracking leads to the use of larger quantities of hydrogen with increased manufacturing costs and to the formation of products which do 60 not give corresponding benefits in further increases in the yield of olefins.

Any catalyst which is capable of catalysing the hydrogenation of compounds containing aromatic rings without substantial structural alteration or breakdown may be used. Since most feedstocks contain sulphur and nitrogen compounds it is desirable that the catalyst should also possess some tolerance to these materials and their hydrogenation products. Hydrogenation catalysts embodying these requisites include for example nickel/molybdenum/alumina, cobalt/tungsten/alumina, nickel/tungsten/alumina, cobalt/molybdenum/alumina, nickel/cobalt/molybdenum/alumina, cobalt/molybdenum/silica/alumina, nickel/molybdenum/silica/alumina, cobalt/tungsten/silica/alumina and nickel/tungsten/silica/alumina. Particularly active hydrogenation catalysts are nickel/tungsten/silica/alumina and cobalt/molybdenum/alumina of which nickel/tungsten/silica/alumina is preferred.

A typical nickel/tungsten/silica/alumina catalyst may have the composition 1–6 per cent by weight of nickel and 9–27 per cent by weight of tungsten, with a silica to alumina ratio in the range 90:10 to 25:75 but compositions outside this range are also effective. Cobalt-/molybdenum/alumina catalysts produced commercially may contain up to 0.5% silica.

The catalyst may conveniently be prepared by impregnating the support with an aqueous solution of a salt of each of the metals, either consecutively or simul-20 taneously. Thus nickel may be added in the form of nickel nitrate, tungsten as ammonium metatungstate, cobalt as cobalt nitrate, acetate etc. and molybdenum as ammonium molybdate. It will usually be found convenient to impregnate the support first with the salt of the metal which is to be present in the highest concentration in the finished catalyst though this is not essential. Other methods of preparing the catalyst include precipitating the metals on the support from a solution of their salts and co-precipitation of the metals with the hydrated support material.

It is preferred that the catalysts be activated before use in the reaction by contact with a stream of hydrogen at a temperature in the range 100° to 800°C, more preferably 300° to 600°C for a period of 1 minute to 24 <sup>35</sup> hours.

Although the metallic components of the aforementioned hydrogenation catalysts are defined in terms of the elemental metals present therein, after activation, at least, the metals will be present in the form of oxides. 40 The precise nature of the active species in the hydrogenation catalysts after contact for some time with the atmospheric petroleum residue feedstock under hydrogenation conditions is now known, though it is possible that they contain in addition to the support, elemental metal, metal oxides, metal sulphides and complex aluminium or silicon/metal compounds.

Although it will usually be convenient to employ the hydrogenation catalyst without prior exposure to materials containing sulphur at least initially, the catalyst may also be used in the sulphided form. The sulphided form of the catalyst may conveniently be prepared by passing hydrogen through liquid tetrahydrothiophene and then over the catalyst maintained at a temperature in the range 100°C to 800°C, preferably 300°C to 600°C for a period of 1 minute to 24 hours.

Using nickel and cobalt catalysts the hydrogenation temperature may be in the range 50° to 500°C, preferably 300° to 400°C and the pressure may be in the range 50 to 500 psig. preferably 200 to 3000 psig.

The hydrocarbon Liquid Hourly Space Velocity (LHSV) may be in the range 0.1 to 5.0 preferably 0.1 to 2.0, even more preferably 0.1 to 0.5. For catalysts other than those containing cobalt or nickel the reaction conditions may be different.

Hydrogen is preferably fed to the hydrogenation zone at about 5 to 10 times the molar rate of the atmospheric petroleum residue feedstock. The major portion of the gaseous phase containing hydrogen may be separated from the liquid phase containing hydrocarbons in a high pressure separator and recycled either directly or, after scrubbing to remove hydrogen sulphide and ammonia, to the hydrogenation zone. Hydrogen dissolved in the liquid phase may be separated in a low pressure separator and either recycled to the hydrogenation zone or used as fuel gas.

10 Whilst the process will normally be operated continuously other methods of operation may also be used such as batch operation in an autoclave.

Hydrogenation may be carried out in a single stage or in a series of two or more operations using the same or different catalysts

Thermal cracking of the distillate fraction in the presence of steam may suitably be effected at a steam to hydrocarbon weight ratio of about 0.5:1 to 2.0:1 in a heated zone, preferably a tube, at a maximum temperature in the range 700° to 1000°C with a residence time in the temperature range between 0.01 and 5 seconds, preferably 0.1 to 2.0 seconds. The products may be rapidly cooled in a heat exchange system and separated and purified by conventional means.

Normally gaseous olefins e.g. ethylene and propylene are used as feedstocks for the production of a wide variety of chemical and polymeric products.

The process of the invention is illustrated by the following Examples:

#### COMPARISON TEST

A sample of Kuwait atmospheric residue with a hydrogen to carbon ratio of 1.59 and a sulphur content of 4.26 per cent weight was vacuum distilled. The initial boiling point of the atmospheric residue was 296.5°C, and 54 per cent volume distilled up to a cut-point temperature of 550°C (corrected to atmospheric pressure). The distillate had a hydrogen to carbon atomic ratio of 1.70 and a sulphur content of 3.15 per cent weight. Analysis indicated that the carbon content in aromatic rings was 19.0 per cent weight of the total carbon, whereas the atmospheric residue contained 18.8 per cent weight of aromatic carbon.

This vacuum distillate was steam cracked in an 8 ml. quartz reactor at a maximum temperature of  $830^{\circ}$ C. The steam to hydrocarbon feed weight ratio was 1.0 to 1.0 with an average hydrocarbon feed rate of 27 g. per hour. The ethylene and propylene yields were 23 and 10 per cent weight on feed respectively with a total conversion to cracked gas of 53 per cent weight on feed.

This example is provided for purposes of comparison and is not an example according to the invention.

#### EXAMPLE 1

A 300 g sample of the Kuwait atmospheric residue used in the comparison test was hydrogenated in a 1 litre rocking autoclave at 370°C under 2500 psig. of hydrogen during 24 hours using 75 g of a cobalt oxide/molybdenum oxide/alumina catalyst. The catalyst containing 3.9 per cent weight cobalt, 19.7 per cent weight molybdenum, and less than 0.1 per cent weight silica, and after calcination in air at 550°C for 2 hours was activated in a stream of hydrogen at 400°C for 24 hours. The recovered hydrogenated atmospheric residue had a hydrogen to carbon atomic ratio of 1.86 and a sulphur content of 0.14 per cent weight. Analysis indicated that the carbon content in aromatic rings was 8.5 per cent weight of the total carbon. This material was vacuum distilled; the initial boiling point of the distillate was 230°C, and 72 per cent volume distolled up to a cut-point temperature of 550°C (corrected to atmo- 5 spheric pressure). The distillate had a hydrogen to carbon atomic ratio of 1.88 and a sulphur content of 0.15 per cent weight. Analysis indicated that the carbon content in aromatic rings was 10.8 per cent weight.

The vacuum distillate was steam cracked under the 10 same conditions as were used in the comparison test. The ethylene and propylene yields were 24 and 11 per cent weight on feed respectively with a total conversion to cracked gas of 57 per cent. There was also a substantial reduction in the coke and tar deposited in the reac-15 tor system compared with that formed from the untreated vacuum distillate.

#### **EXAMPLE 2**

A 300 g sample of the Kuwait atmospheric residue 20 used in the comparison test was hydrogenated in a 1 litre rocking autoclave at 370°C under 2500 psig. of hydrogen during 24 hours using 54.5 g. of a nickel oxide/tungsten oxide/silica/alumina catalyst. The catalyst weight tungsten and the silica to alumina ratio was 3:1. The catalyst was again first calcined in air at 550°C for 2 hours and then immediately before use it was activated at 400°C in a stream of hydrogen for 24 hours. The recovered hydrogenated atmospheric residue had 30 a hydrogen to carbon atomic ratio of 1.79 and a sulphur content of 0.28 per cent weight. Analysis indicated that the carbon content in aromatic rings was 11.5 per cent weight of the total carbon. This material was vacuum distilled; the initial boiling point of the dis- 35 tillate was 229°C, and 80 per cent volume distilled up to a cut-point temperature of 550°C (corrected to atmospheric pressure). The distillate had a hydrogen to carbon atomic ratio of 1.78 and a sulphur content of 0.21 per cent weight. Analysis indicated that the car- 40 drogenation catalyst is nickel/tungsten/silica/alumina. bon content in aromatic rings was 12.4 per cent weight.

This vacuum distillate was steam cracked under the same conditions as were used in the comparison test. The ethylene and propylene yields were 251/2 and 12 per cent weight on feed respectively with a total con- 45 version to cracked gas of 58 per cent. There was a further reduction in the coke and tar deposited in the reactor system compared with that formed in Example 1.

The Examples show that hydrogenation of the atmospheric residue leads to a substantial increase in the 50 percentage of vacuum distillate recoverable as feedstock for thermal cracking. When combined with the increased yield and conversion to ethylene and propylene in the thermal cracking step it can be seen that the increased.

I claim:

1. A process for the production of normally gaseous olefins from an atmospheric petroleum residue feedstock which process comprises the steps of:

a, contacting the petroleum residue feedstock in a hydrogenation zone with a hydrogenation catalyst selected from nickel/molybdenum/alumina, cobalt-/tungsten/alumina, nickel/tungsten/alumina, cobalt/molybdenum/alumina, cobalt/molybdenum/denum/alumina, silica/alumina, nickel/molybdenum/silica/alumina, nickel/tungsten/silica/alumina and hydrogen at a temperature in the range 50° to 500°C, a pressure in the range 50 to 5,000 psig, a Liquid Hourly Space Velocity in the range 0.1 to 5.0, and a hydrogen feed rate of 5 to 10 times the molar feed rate of the atmospheric petroleum residue feedstock, to effect hydrogenation of aromatic hydrocarbons,

- b. separating from the resulting hydrogenated atmospheric petroleum residue feedstock a gaseous phase containing hydrogen and a liquid phase containing hydrocarbons,
- c. recycling at least a portion of said gaseous phase containing hydrogen to said hydrogenation zone,
- d. separating said liquid phase containing hydrocarbons into a distillate fraction having a boiling range below 650°C and a residue fraction having a boiling range above that of the distillate fraction,
- e. subjecting said distillate fraction in the presence of steam to thermal cracking in a pyrolysis zone under conditions effecting conversion of at least a portion of said liquid phase to normally gaseous olefins and
- f. recovering the normally gaseous olefins from the pyrolysis zone effluent.

2. A process according to claim 1 wherein the whole contained 4.9 per cent weight nickel, 15.9 per cent 25 of said liquid phase containing hydrocarbons is, after separation of a gaseous phase containing hydrogen, fed in the presence of steam directly to the pyrolysis zone wherein unvapourised feedstock is removed as a residue fraction in a separation zone prior to entry of the vapourised distillate fraction into that region of the pyrolysis zone maintained under conditions which effect thermal cracking.

> 3. A process according to claim 1 wherein the separation of said liquid phase containing hydrocarbons into a distillate fraction having a boiling range below 650°C and a residue fraction having a boiling range above that of the distillate fraction is effected by vacuum distillation.

> 4. A process according to claim 1 wherein said hy-

5. A process according to claim 1 wherein said hydrogenation catalyst is cobalt/molybdenum/alumina.

6. A process according to claim 1 wherein said hydrogenation catalyst is activated before use in the hydrogenation reaction by contact with a stream of hydrogen at a temperature in the range 100° to 800°C for a period of 1 minute to 24 hours.

7. A process according to claim 1 wherein the temperature is in the range 300° to 600°C, the pressure is in the range 200 to 3,000 psig and the Liquid Hourly Space Velocity is in the range 0.1 to 0.5.

8. A process according to claim 1 wherein the major portion of the gaseous phase containing hydrogen is separated from the liquid phase containing hydrocaroverall yield of normally gaseous olefins is substantially 55 bons in a high pressure separator and recycled either directly or, after scrubbing to remove hydrogen sulphide and ammonia, to the hydrogenation zone.

> 9. A process according to claim 1 wherein the hydrogenation zone is a single zone or a series of zones em-60 ploying the same or different hydrogenation catalyst.

10. A process according to claim 1 wherein thermal cracking of the distillate fraction in the presence of steam is effected at a steam to hydrocarbon weight ratio of 0.5:1 to 2.0:1 in a heated zone at a maximum nickel/cobalt/molyb- 65 temperature in the range 700° to 1,000°C with a residence time in this range between 0.01 and 5 seconds.