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[54] **PYROLYSIS OF HYDROTREATED FEEDSTOCKS**

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[58] **Field of Search** 260/683, 680, 673.5; 208/57, 208/89

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[57] **ABSTRACT**

Heavy hydrocarbon feedstocks are subjected to a hydrogenation pre-treatment prior to pyrolysis, said hydrogenation step being so controlled as to avoid hydrocracking and being carried out at a temperature of from about 640° to about 800° F and at a pressure of from about 750 to about 1,250 psig when a significantly increased yield of mononuclear aromatics is desired and at a pressure of from about 1,250 to about 3,000 psig when a significantly increased yield of 1,3-butadiene is desired.

17 Claims, No Drawings

PYROLYSIS OF HYDROTREATED FEEDSTOCKS

BACKGROUND

In the well-known process involving the pyrolysis of hydrocarbons for the preparation of the lighter olefins, such as ethylene, propylene, etc., there is a pronounced trend toward the employment of heavier feedstocks based on considerations of availability and economics.

However, with the increase in molecular weight of the feedstock, there is a concomitant increase in sulfur content together with a decrease in the ratio of hydrogen to carbon due to the greater aromatic hydrocarbon content of the feedstock. The higher sulfur content causes corrosion in the tubes of the furnace and is obviously undesirable. The higher aromatic hydrocarbon content, in particular, that of the polynuclear aromatic hydrocarbons, results in tendency toward the production of heavy tarry materials and coke. The production of such substances is likewise clearly undesirable in a pyrolysis plant.

It is furthermore well known that butadiene can be more economically produced as a by-product from the pyrolysis of hydrocarbon feedstocks than it can be by the direct dehydrogenation of butanes or butenes. It has been observed that as the molecular weight of the feedstock undergoing pyrolysis increases, the yield of butadiene increases with a concomitant decrease in the ratio of ethylene to butadiene produced. However, the increase in sulfur content which accompanies an increase in molecular weight of the feedstock, as noted above, presents a problem in the removal of sulfur from the system. While certain expedients are available to the art for the removal of sulfur, such expedients in general suffer from disadvantages which render them unsatisfactory for use. Thus, the use of a simple caustic wash for removal of the sulfur content from a pyrolysis gas becomes uneconomical when the sulfur content exceeds about 0.5 percent. The use of a regenerative amine system gives rise to polymer formations resulting in undesirable plugging of towers and coating of reboilers. Hence, it is desirable to provide a method for the pre-treatment of heavier feedstocks which will eliminate the problems encountered in sulfur removal systems.

The production of particular products from a pyrolysis process has hitherto generally required the selection and use of specific feeds depending on the particular product distribution sought. The desirability of providing a means whereby the same feedstock can be selectively pretreated to increase the production of particular different end products upon pyrolysis is self-evident.

SUMMARY OF THE INVENTION

The present invention relates to and has for its object the provision of a method of pretreating hydrocarbon feedstocks whereby upon pyrolysis such pretreated feedstocks will provide improved yields of particular predetermined products.

In accordance with the present invention, heavy hydrocarbon feedstocks, particularly virgin gas oil stocks, are subjected to hydrogenation prior to pyrolysis. The conditions of hydrogenation are carefully controlled so that no significant hydrocracking occurs. The effect of the controlled hydrogenation process disclosed and claimed herein is to saturate the aromatic hydrocarbons present in the feedstock and to remove the sulfur present therein.

The hydrogenation is carried out at a temperature of from about 640° to about 800°F, preferably at from about 650° to about 740°F. This temperature range is suitable and is employed for the hydrogenation of the feedstock, irrespective of the particular end product desired, that is, in the production of either increased yields of benzene-toluene-xylene aromatics or of 1,3-butadiene.

Where increased production of aromatic products is intended, pressures of from about 750 to about 1,250 pounds per square inch and preferably from about 750 to about 1,000 pounds per square inch are employed at a recycle hydrogen rate of 500 to 1,500 SCF per barrel, preferably 3,900 to 13,200 SCF per barrel and at a liquid space velocity per hour of 0.5 to 3,0, preferably 0.8 to 1.7.

Where increased production of 1,3-butadiene is desired, increased pressures of from about 1,250 to about 3,000 pounds per square inch, preferably from about 1,500 to about 2,000 pounds per square inch, are employed at a space velocity of 0.5 to 3.0, preferably 0.8 to 1.7. From the foregoing, it will be seen that the differentiating condition, determining the direction in which the process will go resides in the hydrogen partial pressure, or in effect the total pressure.

In summary, by subjecting a hydrocarbon feedstock having a boiling range of from about 400 to about 1,100°F, an API gravity of about 18 to about 45 and a molecular weight of at least about 180 to carefully controlled conditions of hydrogenation, removal of sulfur can be effected, the formation of undesirable residues can be suppressed, and the same hydrocarbon feedstock can be employed for the selective production of increased yields of either benzene-toluene-xylene aromatics or of 1,3-butadiene as by-products in the pyrolysis of the feedstock to produce light olefins.

As a further advantage of the present process, it has been found that the yields of ethylene will be increased, the extent of the increase depending on the amount of hydrogen which has been picked up by the feedstock during pretreatment.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In carrying out the present invention a middle distillate or gas oil fraction and hydrogen, individually or as a mixture, are charged to a suitable reaction vessel in which contact is effected with a catalyst contained therein, as for example, in one or more fixed beds in a reaction zone in the vessel. The effluent from the reaction vessel is cooled and passed to a separator where it is separated into a normally liquid stream comprising the hydrogenated product and a normally gaseous stream comprising chiefly hydrogen. The latter is advantageously recycled to the hydrotreater to make up a portion of the hydrogen which is charged to the vessel.

As noted, the process is effected in the presence of a suitable catalyst. Broadly, the catalyst employed will comprise one or more metals from the groups VI*b* and/or VIII, on a support such as alumina, titania or silica-alumina. Illustratively, the catalyst comprises such metals as cobalt, molybdenum, nickel, tungsten, palladium, platinum and chromium. In particular, it has been found that the following catalysts are particularly suited for use in the pre-treatment of heavy feedstocks; nickel-molybdenum on alumina, nickel-tungsten on alumina and cobalt-molybdenum on alumina.

In the practice of the pre-treatment step of the present invention, a temperature of from about 640° to about 800°F is employed. While temperatures below 640°F could be employed, it has been found that at such lower temperatures the reaction rates achieved are not practicable for commercial utilization. At temperatures above about 800°F, hydrocracking reactions will occur thus reducing the efficiency of the process, increasing hydrogen consumption and reducing the yield of the desired benzene-toluene-xylene aromatic or 1,3-butadiene by-product. The preferred temperature range is from about 650° to about 740°F.

While the general range of operating temperature and space velocity of the hydrogenation is the same, irrespective of the particular end products desired, the pressure is varied to achieve the desired selectivity. Where the production of an end product of increased benzene-toluene-xylene aromatics content is intended, pressures of from about 750 to about 1,250 psig are employed. Preferably, the pressure will be from about 750 to about 1,000 psig. Where an end product having an increased 1,3-butadiene content is desired, the pressure is increased. Thus, for the increased production of 1,3-butadiene, a pressure of from about 1,250 to about 3,000 psig will be suitable, with the preferred ranges being from about 1,500 psig to about 2,000 psig.

The feedstock employed is a straight run kerosene or gas oil feedstock having a molecular weight of at least 180, a boiling range within the range of from about 400° to about 1,100°F, an API gravity of from about 18 to about 45 and a total aromatics content of about 20–60 percent, of which approximately one-half comprises mononuclear aromatic substances. Exemplary of the feedstocks which can be employed is a vacuum gas oil stock having an API gravity at 60°F of 22.5, a molecular weight of 455, an ASTM boiling range of 630° to 1,080°F and a total aromatics content of 43 percent. Examples of other suitable feedstocks are gas oils of various boiling ranges within the broad range of 400° to 1,100°F, including light, medium, heavy and vacuum gas oils. Any gas oil having the boiling range and gravity characteristics set forth above can be pretreated in accordance with the present invention.

Thus, it will be seen that by appropriately controlling the conditions of the pre-treatment step of hydrogenation, the product distribution of the end product can be controlled so that from the same feedstocks, end products containing either significantly increased benzene-toluene-xylene aromatics content or 1,3-butadiene content can be obtained.

The pretreated feedstocks are subjected to pyrolysis under conventional operating conditions and in accordance with known techniques. The product distribution upon pyrolysis is dependent upon the particular conditions employed in the pretreatment step as discussed earlier. The increase in yields of benzene-toluene-xylene aromatics or of 1,3-butadiene together with the increase in yields of ethylene and propylene greatly enhances the economics of the production of the lighter olefins, such as ethylene and propylene, from heavier hydrocarbon feedstocks.

A further advantage of the process of the present invention resides in its ready adaptability for integration into a pyrolysis process for the production of the lighter olefins from heavy hydrocarbon feedstocks. Such integration avoids the necessity for several steps common to the hydrotreating of petroleum fractions together with the process equipment involved. Thus, the step of cooling the liquid portion of the reactor effluent from the hydrogenation can be eliminated together with the required product coolers, since the liquid reactor effluent can flow directly to pyrolysis. Similarly, stabilization and stripping of dissolved H_2S can be dispensed with, together with the equipment required for these operations, since pretreatment in accordance with the present invention brings the level of dissolved H_2S below that which would be formed during pyrolysis of untreated feedstocks. Direct feeding of the hot hydrotreated product into the pyrolysis zone avoids the necessity for additional heater charge pumps. Further, overall fuel and heat requirements are diminished, the fuel fired in the pretreatment stage will provide sensible heat in the pyrolysis stage and since the heat of hydrogenation is substantial, it will lessen fuel requirements in the pyrolysis stage. Finally, hydrogen produced in the pyrolysis stage can be employed as makeup hydrogen in the pretreating stage. All of these factors contribute toward a greater efficiency and greater economy in the production of ethylene and propylene from the heavier hydrocarbon feedstocks.

The invention is further illustrated by the following Examples but the scope of the invention is not to be limited thereby.

EXAMPLE I

A heavy vacuum gas oil feedstock having the properties set forth in Table I is hydrogenated in accordance with the conditions of Table II to yield a stock having the properties set forth in Table III.

TABLE I

Gravity, °API	22.5
B.P. range	630–1080°F
Molecular Weight	475
Conradson Carbon wt.%	.75
Pour Point	110°F
Aniline Point	198°F
Sulfur, wt.%	.73
Nitrogen, wt.%	.10
Total aromatics and Polar Compounds wt.%	42.50

TABLE II

System Pressure	1000 psig
Catalyst Bed Temperature	700°F
Liquid Hourly Space Velocity	1.6
Hydrogen Recycle Rate	8500SCF/Bbl
Hydrogen Consumption	200 SCF/BbL.

The catalyst employed is a 3.8 percent nickel oxide, 16.8 percent molybdenum oxide on an alumina support, activated by presulfiding with a 10 percent H_2S/90 percent H_2 stream for 2 hours at 700°F.

TABLE III

Gravity, °API	24.8
B.P. range	530–1090°F
Molecular Weight	443
Conradson Carbon wt.%	.15
Pour Point	115°F
Aniline Point	204°F
Sulfur, wt.%	.11
Nitrogen, wt.%	.06
Total aromatics wt.%	38.3

EXAMPLE II

Both the untreated stock and the hydrotreated product of Example I are subjected to pyrolysis under equivalent conditions of maximum cracking severity as shown in Table IV.

TABLE IV

	Maximum Severity Treated	Untreated
Test Period, Hrs.	5	5
Steam/Hydrocarbon Ratio, wt.	1.04	1.01
HC Partial pressure at inlet,psia	2.39	2.39
HC partial pressure at outlet, psig	8.83	8.46
Exit Tube Wall Temperature, °F	1539	1530
Outlet Fluid Temperature, °F	1505	1464
Percent Feed Recovery, wt.	99.0	98.5
Percent Hydrogen in C_5+ liquid, wt.	8.04	8.05

By equivalent conditions of maximum cracking severity is meant that the hydrogen content of the pyrolysis C_5+ liquid product is controlled to about the same value as close to the operational coking limit.

The results of the pyrolysis are recorded in Table V, in which the yield structures for the two stocks are shown in terms of weight percent on feed.

TABLE V

Operation	Maximum Severity Treated	Untreated		Yield Difference at Maximum Severity Absolute	Percent
Hydrogen	0.50	0.43			
Methane	8.71	7.80			
Ethane	2.96	3.00			
Ethylene	18.63	17.18		+1.45	+8.5
Acetylene	0.22	0.14			
Propane	0.32	0.35			
Propylene	13.30	13.12		+0.18	+1.4
Propadiene	0.24	0.17			
Methyl Acetylene	0.30	0.19			
Butanes	0.09	0.11			
Butenes	5.59	6.60			
1,3-Butadiene	5.57	5.32		+0.25	+4.7
Ethyl Acetylene	0.06	0.01			
C5's	4.38	5.21			
Benzene	4.54	3.00	AROMATICS		
Toluene	3.08	2.74			
Ethyl Benzene	0.39	0.39		+2.30	+30.3
Xylenes	1.10	1.03			
Styrene	0.79	0.44			
Non-aromatic gasoline component	3.73	4.89			
Pyrolysis gas oil and residue	25.50	27.88			
Total:	100.00	100.00			

The pyrolysis results recorded above demonstrate that significant increases in benzene-toluene-xylene aromatics are realized by the practice of the pretreatment step.

EXAMPLE III

A gas oil feedstock having the properties set forth in Table VI is hydrogenated in accordance with Table VII to yield a stock having the properties set forth in Table VIII.

TABLE VI

Gravity, °API	34
Boiling Point Range, ASTM	350–625°F
Molecular Weight	234
PONA - Analysis, Wt.%	
Paraffins	38
Naphthenes	32
Aromatics	30

TABLE VII

System Pressure	2500 psig
Catalyst Bed Temperature	675°F
Liquid Hourly Space Velocity	1.0
Hydrogen Recycle Rate	8500 SCF/BbL

The catalyst employed is the same as that set forth in Table II.

TABLE VIII

Gravity, °API	44
Boiling Point Range	340–640°F
Molecular Weight	202
PONA-Analysis, Wt.%	
Paraffins	40
Naphthenes	55
Aromatics	5

EXAMPLE IV

Both the untreated feedstock and the hydrotreated product of Example III are subjected to pyrolysis under equivalent conditions of maximum cracking severity as set forth in Table IX.

TABLE IX

	Treated	Untreated
Test Period, Hrs.	5	5
Steam/Hydrocarbon Ratio, Wt.	1.10	1.10
HC partial pressure at inlet psia	5.4	5.4
HC partial pressure at outlet psia	12.0	11.9
Outlet Fluid Temp. °F	1526	1504
Percent H_2 in C_5 + Liquid Wt.	7.95	7.73

The results of the pyrolysis are recorded in Table X.

TABLE X

Pyrolysis Yield (Wt.%)

Operation	Maximum Severity Treated	Untreated		Yield Difference Absolute	Percent
Hydrogen	0.83	0.63			
Methane	13.06	11.20			
Ethane	3.07	3.06			
Ethylene	28.20	23.64		+4.56	+19.3
Acetylene	0.50	0.22			
Propane	0.14	0.45			
Propylene	14.90	15.07		−0.17	−1.1
Propadiene	0.43	0.37			
Methyl Acetylene	0.16	0.28			
Butanes	0.08	0.09			
Butenes	4.37	4.67			
1,3-butadiene	6.35	3.50		+2.85	+81.4
C_5's	1.73	1.56			
Benzene	4.42	5.00	AROMATICS		
Toluene	2.37	2.75			
Ethyl Benzene	.27	0.27		−1.30	−13.0
Xylenes	1.08	1.21			
Styrene	0.57	0.78			
Non-aromatic gasoline component	8.90	5.88			
Pyrolysis gas oil + Residue	8.57	19.37			
Total:	100.00	100.00			

We claim:

1. In a process for the pyrolysis of a heavy hydrocarbon feedstock having a boiling range within the range

of from about 400°F to 1,100°F, the improvement which comprises selectively hydrogenating said feedstock prior to pyrolysis to effect the production of pyrolysis products having varied aromatic content and 1,3-butadiene content by subjecting said feedstock to hydrogenation in contact with a catalyst comprising a member selected from the group consisting of Group VI*b* metals, Group VIII metals and mixtures thereof, at a temperature of from about 640° to 800°F and a liquid hourly space velocity of from about 0.5 to about 3.0 and selectively at a pressure of from about 750 to about 1,250 psig where a pyrolysis product of increased aromatic content is desired and to a pressure of from about 1,250 to about 3,000 psig where a pyrolysis product of increased 1,3-butadiene content is desired.

2. In a process for the pyrolysis of a heavy hydrocarbon feedstock having a boiling range within the range of from about 400°F to about 1,100°F, the improvement which comprises selectively hydrogenating said feedstock prior to pyrolysis to increase the yield of aromatic hydrocarbons by subjecting said feedstock to hydrogenation in contact with a catalyst comprising a member selected from the group consisting of Group VI*b* metals, Group VIII metals and mixtures thereof at a temperature of from about 640° to about 740°F and a liquid hourly space velocity of from about 0.5 to about 3.0 and a pressure of from about 750 to about 1,250 psig.

3. In a process for the pyrolysis of a heavy hydrocarbon feedstock having a boiling range within the range of from about 400°F to about 1,100°F, the improvement which comprises selectively hydrogenating said feedstock prior to pyrolysis to increase the yield of aromatic hydrocarbons by subjecting said feedstock to hydrogenating in contact with a catalyst comprising a member selected from the group consisting of Group VI*b* metals, Group VIII metals and mixtures thereof at an average temperature of 700°F, a pressure of about 1,000 psig and a liquid hourly space velocity of 1.6.

4. In a process for the pyrolysis of a heavy hydrocarbon feedstock having a boiling range within the range of from about 400°F to about 1,100°F, the improvement which comprises selectively hydrogenating said feedstock prior to pyrolysis thereof to increase the yield of 1,3-butadiene by subjecting said feedstock to hydrogenation in contact with a catalyst comprising a member selected from the group consisting of Group VI*b* metals, Group VIII metals and mixtures thereof at a temperature of from about 640° to about 740°F and a liquid hourly space velocity of from about 0.5 to about 3.0 and a pressure from about 1250 to about 3,000 psig.

5. In a process for the pyrolysis of a heavy hydrocarbon feedstock having a boiling range within the range of from about 400°F to about 1,100°F, the improvement which comprises selectively hydrogenating said feedstock prior to pyrolysis thereof to increase the yield of 1,3-butadiene by subjecting said feedstock to hydrogenation in contact with a catalyst comprising a member selected from the group consisting of Group VIb metals, Group VIII metals and mixtures thereof at an average temperature of 700°F and a liquid hourly space velocity of 1.6 and a pressure of about 2,500 psig.

6. A process according to claim 2 wherein the catalyst is a sulfided nickel-molybdenum on an alumina support.

7. A process according to claim 2 wherein the catalyst is a sulfided cobalt-molybdenum on an alumina support.

8. A process according to claim 2 wherein the catalyst is palladium on an alumina support.

9. A process according to claim 2 wherein the catalyst is a sulfided nickel-tungsten on an alumina support.

10. A process according to claim 2 wherein the feedstock is a gas oil feedstock having a boiling range within the range of from about 400° to about 1,100°F, an API gravity of from about 18 to about 45 and a total aromatics content of from about 20 to about 60 percent.

11. A process according to claim 3 wherein the feedstock is a heavy vacuum gas oil having an API gravity at 60°F of 22.5, a boiling range of 630° to 1,080°F and a total aromatics content of 43 percent.

12. A process according to claim 4 wherein the catalyst is a sulfided nickel-molybdenum on an alumina support.

13. A process according to claim 4 wherein the catalyst is sulfided cobalt-molybdenum on an alumina support.

14. A process according to claim 4 wherein the catalyst is palladium on an alumina support.

15. A process according to claim 4 wherein the catalyst is a sulfided nickel-tungsten on an alumina support.

16. A process according to claim 4 wherein the feedstock is a gas oil feedstock having a boiling range within the range of from about 400° to about 1,100°F, an API gravity of from about 18 to about 45 and a total aromatics content of from about 20 to about 60 percent.

17. A process according to claim 5 wherein the feedstock is a gas oil feedstock having an API gravity at 60°F of 34, a boiling range of 300° to 735°F and a total aromatics content of 30 percent.

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