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54 **Conversion increase of vacuum residuums.**

57 The conversion of a vacuum residuum feed in a hydrocracking operation comprising hydrocracking said feed vacuum residuum in a hydrocracking zone, recovering and separating distillates from the hydrocracking zone, and recycling a stream of unconverted vacuum residuum bottoms to the hydrocracking zone, can be increased by deasphalting unconverted vacuum residuum bottoms in the recycle stream by treatment in an extraction zone with a cosolvent (e.g. n-heptane) at ambient or elevated temperature, and a pressure sufficient to maintain the cosolvent in the liquid state. The most undesirable sediments are selectively removed from said unconverted vacuum residuum bottoms to increase the conversion of said vacuum residuum feed.

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## CONVERSION INCREASE OF VACUUM RESIDUA

This invention relates to a process for the conversion of vacuum residua in a hydrocracking operation. More particularly, it relates to the treatment of unconverted vacuum residua to remove the most undesired asphaltenic materials therefrom in order to increase the conversion of the vacuum residue virgin feed.

In converting heavy vacuum residua, e.g., in a hydrocracking operation, a problem with obtaining a  
 5 good or better conversion is the amount of asphaltenes or asphaltenic materials which are deficient in hydrogen and have a high trace metals content. In selectively removing a major portion of the more hydrogen deficient asphaltenes from the unconverted 1000° F plus material, the effective conversion of the remaining 1000° F material, as well as the original vacuum residuum chargestock, may be significantly enhanced.

10 Thus, it is an object of the present invention to provide a means of treating the unconverted vacuum bottoms to obtain the optimum conversion of virgin vacuum residuum.

U.S. Patent Re. 32,265 discloses a hydrogenation process using at least one fluidized catalytic stage and a recycle material of heavy hydrogenated effluent. The heavy effluent material is cooled to a temperature within 350-600° F to separate toluene and heptane insoluble coke precursors prior to recycle.  
 15 This separation may be enhanced by the use of centrifugation, filtration or a bed of particulate material, e.g., calcined coke.

U.S. Patent 4,411,768 discloses a higher conversion in a process for upgrading high boiling hydrocarbon materials to valuable lower boiling hydrocarbon materials in an ebullated catalytic bed wherein recycle is recovered from the upgraded product and at least 25 percent by volume of the recycle is comprised of  
 20 the 950° F plus components of the product. The liquid recycle is cooled to a temperature of 350° F to 700° F to separate coke precursors from the liquid recycle on a bed of particulate solids prior to recycling it back to the hydrogenation zone.

U.S. Patent 4,305,814 discloses an energy efficient process for separating a hydrocarbonaceous material into various fractions employing solvents at elevated temperatures and pressures. The  
 25 solvent composition comprises at least one member selected from the group of paraffinic hydrocarbons containing from 3 through 9 carbon atoms, mono-olefin hydrocarbons containing from 4 through 8 carbon atoms, aromatic hydrocarbons having a normal boiling point temperature below about 350° F and alcohols containing from 3 through 9 carbon atoms. The particular amount of asphaltenes or sediment that should be removed to obtain a deasphalted oil that has excellent recycle properties is not disclosed.

30 U.S. Patent 4,502,944 discloses a method of separating a process material comprising oils, resins and asphaltenes into at least three fractions. Method employs light organic solvents (paraffinic hydrocarbons preferably having between 3 and 8 carbon atoms in a solvent/process material ratio of at least about 3:1) under elevated temperature and pressure conditions. As in U.S. Patent 4,305,814, the particular amount of asphaltenes or sediment that should be removed to obtain a deasphalted oil that has excellent recycle  
 35 properties is not disclosed.

U.S. Patent 3,412,010 discloses that the conversion of a vacuum residuum in a hydrocracker is improved by recycling the 680-975° F cut and the 975° plus residue back to the reactor. No mention of removing coke precursors or asphaltenes in the recycle streams is provided.

40 U.S. Patent 3,905,892 discloses a process for hydrocracking vacuum residuum wherein the 975° F plus product may be recycled after removing the asphaltenes. The latter is partially oxidized to yield hydrogen for providing make-up hydrogen for the hydrocracking reactor. The effect of deasphalting conditions on product yields when the deasphalted oil is recycled is not disclosed.

U.S. Patent 4,457,830 discloses the use of inorganic acids for precipitating and decomposing preasphaltenes and coprecipitating solids. The effect of deasphalting conditions on product yields when the  
 45 deasphalted oil is recycled is not disclosed.

The present invention provides an improvement in a method for conversion of a vacuum residuum feed in a hydrocracking operation which comprises upgrading the vacuum residuum feed, recovering and separating distillates from the remaining vacuum residuum feed and recycling unconverted vacuum residuum bottoms to the upgrading zone. The improvement comprises deasphalting the unconverted  
 50 asphaltene-containing unconverted vacuum residuum bottoms in the recycle stream by treating said unconverted vacuum residuum bottoms in an extraction zone with a cosolvent under ambient conditions to a related temperature (and sufficient pressure wherein the recycle stream and cosolvent are maintained in a liquid state), whereby the most undesirable hydrogen deficient asphaltenes are selectively removed from the unconverted vacuum residuum bottoms to increase the overall conversion of the vacuum residuum feed.

The present invention for improving the conversion of a virgin vacuum residuum into a useful product

suggests the treatment of the unconverted vacuum bottoms after separating it from the cracked reaction distillate product in the reactor effluent. Then the treated vacuum bottoms, less the most undesirable hydrogen deficient asphaltenes and a majority of the trace metals, is recycled back to the reaction zone to be converted to additional quantities of the desired distillate products, i.e. naphtha, diesel fuel and vacuum gas oil. The latter stream is used to make additional naphtha and diesel fuel by using it as a charge stock component for a fluidized catalytic cracking unit.

In the overall process of converting a vacuum residuum feed into the desired distillates, the improvement provided by the present invention is the treatment of the unconverted vacuum bottoms with a cosolvent to selectively remove most of the undesirable hydrogen deficient asphaltenes from the vacuum bottoms prior to their being recycled to the reactor, i.e., reaction zone, for further hydrocracking.

As a result of the cosolvent treatment, the amount of the most undesirable hydrogen deficient asphaltenes to be selectively removed ranges from about 10 percent to about 20 percent.

In treating the unconverted vacuum bottoms with a cosolvent, the amount of cosolvent used is defined as the volume ratio of cosolvent to unconverted vacuum bottoms and ranges from about 1:1 to about 40:1.

The cosolvents that may be used according to the present invention include individual solvents such as n-pentane or n-heptane or (C<sub>5</sub>-C<sub>7</sub>) paraffines or a mixture of (C<sub>5</sub>-C<sub>6</sub>) naphthenes and (C<sub>6</sub>-C<sub>7</sub>) aromatics. The aromatics being benzene and toluene.

To illustrate the advantage of deasphalting with n-heptane, a sample of the untreated unconverted vacuum bottoms and various deasphalted oils from the same unconverted vacuum bottoms sample were processed in a continuous stirred tank reactor (CSTR) at a catalyst space velocity of 0.13 bbl/lb/day at successive temperatures of 795, 805 and 815° F over an Mo/A1203 catalyst that mimics the steady-state activity of a commercial NiMo/A1<sub>2</sub>O<sub>3</sub>. The CSTR pressure was held at 2,250 psig with hydrogen and an H<sub>2</sub> treatment rate of 7,000 SCF/bbl. Processing the untreated and unconverted vacuum bottoms and samples of the same unconverted vacuum bottoms individually deasphalted with toluene, cyclohexane and n-heptane gave the following results:

TABLE I

SAMPLE	TEMPERATURE (° F)	CALCULATED OVERALL CONVERSION 1000 ° F PLUS BOILING POINT MATERIAL (wt.%)	PERFORMANCE INDICATORS*	
			Presence of Sediments	Toluene Insolubles (wt.%)
Untreated and unconverted vacuum bottoms	795	33	yes	0.6
	805	38	yes	1.2
	815	47	yes	1.3
Unconverted vacuum bottoms after toluene insolubles	795	39	yes	n.a.
	805	42	yes	1.3
	815	50	yes	1.3
Unconverted vacuum bottoms after removing cyclohexane insolubles	795	41	none	0.3
	805	49	none	0.5
	815	58	yes	0.8
	825	62	yes	0.7
Unconverted vacuum bottoms after removing n-hexane insolubles	795	52	none	0.0
	805	56	none	0.0
	815	65	none	0.0
	825	73	none	n.a.

\* Presence of sediment detected visually through a low power microscope at the end of each sample period (key samples confirmed by taking slide photographs at 600 magnification). Toluene insolubles in total liquid product were measured by Soxhlet extractions.

The above results show that the n-heptane deasphalted vacuum bottoms sample provides a much improved recycle stream for a residuum hydrocracking process designed to upgrade 1000° F and above boiling point components. Not only is the allowable conversion increased at a given temperature but, essentially, no sediment is formed. The latter is very important for reducing catalyst poisoning and minimizing plugging problems on account of sediment formation and deposition in flow control valves, heat exchangers and separation vessels downstream from the reaction zone. In addition, deasphalting the vacuum bottoms recycle stream with n-heptane versus the other solvents allows the reactor temperature to be increased by at least 10° F to further improve hydrocracking conversion without causing additional sediment.

Deasphalting vacuum bottoms with toluene shows a negligible improvement in the overall conversion of the 1000° F plus boiling point components compared with the untreated vacuum bottoms and essentially no improvement in reducing sediment formation as measured by Soxhlet extractions with toluene. The cyclohexane deasphalted vacuum bottoms, on the other hand, provides an intermediate valued recycle stream in that the conversion is significantly improved over the untreated or toluene deasphalted vacuum bottoms but sediment begins to form in the reactor effluent as the reactor temperature is raised to provide a better overall conversion of the components boiling above 1000° F.

It is of interest to note the relative amounts of sediment removed from the particular vacuum bottoms sample (VB) with solvents selected from each of the three basic hydrocarbon types at solvent/VB dosages of 20/1 at ambient conditions:

	Sediment, wt. %
Toluene	< 0.5
Cyclohexane	6 - 7
n-Heptane	15 - 16

It is well known in the art that the lighter the n-paraffin used for deasphalting the more sediment (comprising asphaltenes, other carbonaceous material and trace metals) will be removed from vacuum or atmospheric residuum. For instance, deasphalting the same vacuum bottoms sample with n-pentane removed 20-22 wt. % sediment. The object is to remove as little sediment as possible and still improve the overall conversion of 1000° F plus material while producing no more sediment.

Certainly if the n-heptane deasphalted vacuum bottoms improves conversion without causing any additional sediment, the n-pentane deasphalted vacuum bottoms would do as well but there would be the additional amount of asphaltenes to be disposed of. Consequently, it is proposed that deasphalting with n-heptane provides a standard for determining how much of the asphaltene phase should be removed for a given vacuum bottoms stream if a mixed solvent comprising paraffins and naphthenes with some aromatics is being used.

Another reason for not removing more of the sediment than necessary is to avoid removing the lighter asphaltenes containing a higher proportion of hydrogen and less carbon since the number of condensed aromatics is less. The lighter asphaltenes crack more easily and thereby help to improve the overall conversion of the 1000° F plus boiling point components. Some of the key analytical indicators for the deasphalted vacuum bottom (VB) samples are summarized in Table II:

TABLE II

	Micro Carbon Test, wt. %	Hydrogen/Carbon Weight Ratio	Trace Metal Analyses, ppm	
			Nickel	Vanadium
Untreated VB	22.5	0.1140	28	38
Toluene DAVB	22.3	0.1156	29	28
Cyclohexane DAVB	18.1	0.1211	13	14
n-Heptane DAVB	12.3	0.1341	< 5	2.4
n-Pentane DAVB	10.4	-	< 5	2

In Table III below, samples of untreated and n-heptane deasphalted vacuum bottoms were blended with virgin vacuum residue and processed in a CSTR, as described in the first illustration, to better stimulate a commercial application. The blends were made up of one part untreated VB (or n-heptane DAVB) and two parts by weight of virgin vacuum residue. The results show that as the hydrocracking reactor severity was increased by raising the temperature to 815 °F the n-heptane DAVB allowed the conversion of 1000 °F plus material to be increased without producing any additional sediment. Moreover, by deasphalting the same vacuum bottoms sample with n-heptane the reactor temperature could be raised at least another 10 °F to obtain additional conversion without producing any additional sediment formation.

TABLE III

Sample	Temperature °F	Calculated Overall Conversion of 1000 °F Plus Boiling Point Material (wt.%)	Presence of Sediment
Untreated VB with Virgin VR	795	52	none
	805	55	yes
	815	65	yes
n-Heptane Deasph. VB recycle with Virgin VR	795	51	none
	805	55	none
	815	66	none
	825	70	none

### Claims

1. A method for increasing the conversion of a vacuum residuum feed in a hydrocracking operation which comprises hydrocracking said feed vacuum residuum in a hydrocracking zone, recovering and separating distillates from the hydrocracking zone, and recycling a stream of unconverted vacuum residuum bottoms to the hydrocracking zone characterized by deasphalting unconverted vacuum residuum bottoms in the recycle stream by treatment in an extraction zone with a cosolvent at ambient or an elevated temperature, and a pressure sufficient to maintain the cosolvent in the liquid state, whereby the most undesirable sediments are selectively removed from said unconverted vacuum residuum bottoms to increase the conversion of said vacuum residuum feed.
2. A method according to Claim 1 characterized in that said cosolvent is n-heptane.
3. A method according to Claim 2 characterized in that the volume ratio of n-heptane to unconverted vacuum residuum bottoms is from 1:1 to 40:1.
4. A method according to Claim 1 characterized in that the cosolvent is a mixture of hydrocarbons selected from (C<sub>5</sub>-C<sub>7</sub>) paraffins, (C<sub>5</sub>-C<sub>6</sub>) naphthenes and (C<sub>6</sub>-C<sub>7</sub>) aromatics.

5. A method according to Claim 4 characterized in that the paraffins are n-pentane, n-hexane and n-heptane and the aromatics are toluene and benzene.

6. A method according to any one of Claims 1 to 5 characterized in that the unconverted vacuum residuum bottoms are treated with the cosolvent at a temperature from ambient to 700 °F (371 °C).

5 7. A method according to Claim 6 characterized in that the temperature is from 150 to 650 °F (65.5 to 343 °C).

8. A method according to any one of Claims 1 to 7 characterized in that the pressure is 1 to 60 atmospheres (0.10 to 6.08 MPa).

9. A method according to Claim 8 characterized in that the pressure is from 1 to 40 atmospheres (0.10  
10 to 4.05 MPa).

10. A method according to any one of Claims 1 to 9 characterized in that the amount of the most undesirable hydrogen deficient asphaltenes selectively removed is from 10 to 20 percent.

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# EUROPEAN SEARCH REPORT

Application Number

EP 90 30 5447

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 216 448 (GULF CANADA) * Claims 1-8; page 4, lines 10-19; page 5, lines 20-22; page 6, lines 10-27 * ---	1,2,3,4 ,5,6,7, 8,9	C 10 G 67/04
X,D	US-A-3 905 892 (GREGORI et al.) * Claims 1,2,3; column 3, lines 42-67 * -----	1,2,3,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-09-1990	Examiner DE HERDT O.C.E.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			