

June 10, 1969

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3,449,460

UPGRADING OF COKE OVEN LIGHT OILS

Filed June 6, 1968

Sheet 1 of 2

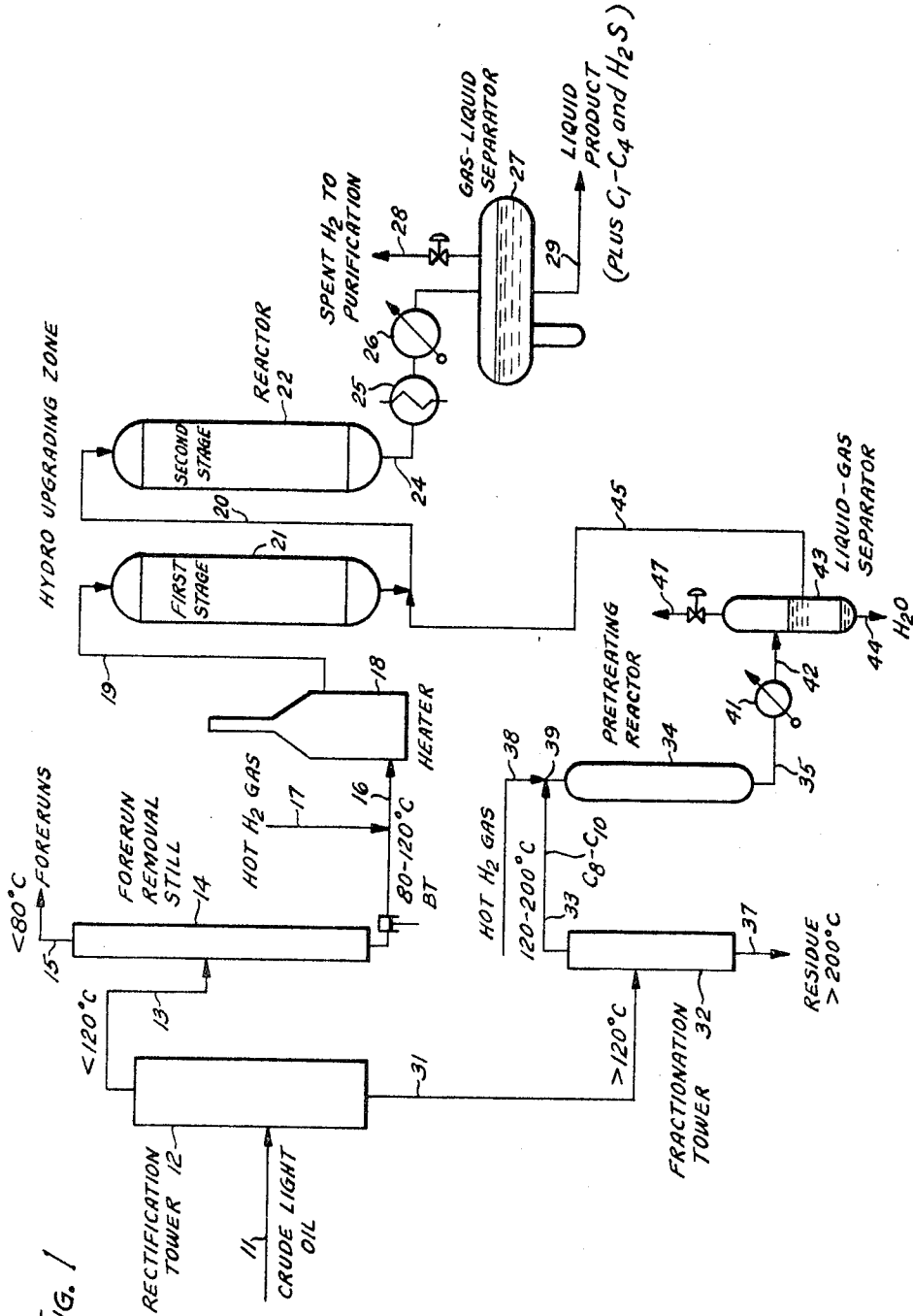


Fig. 1

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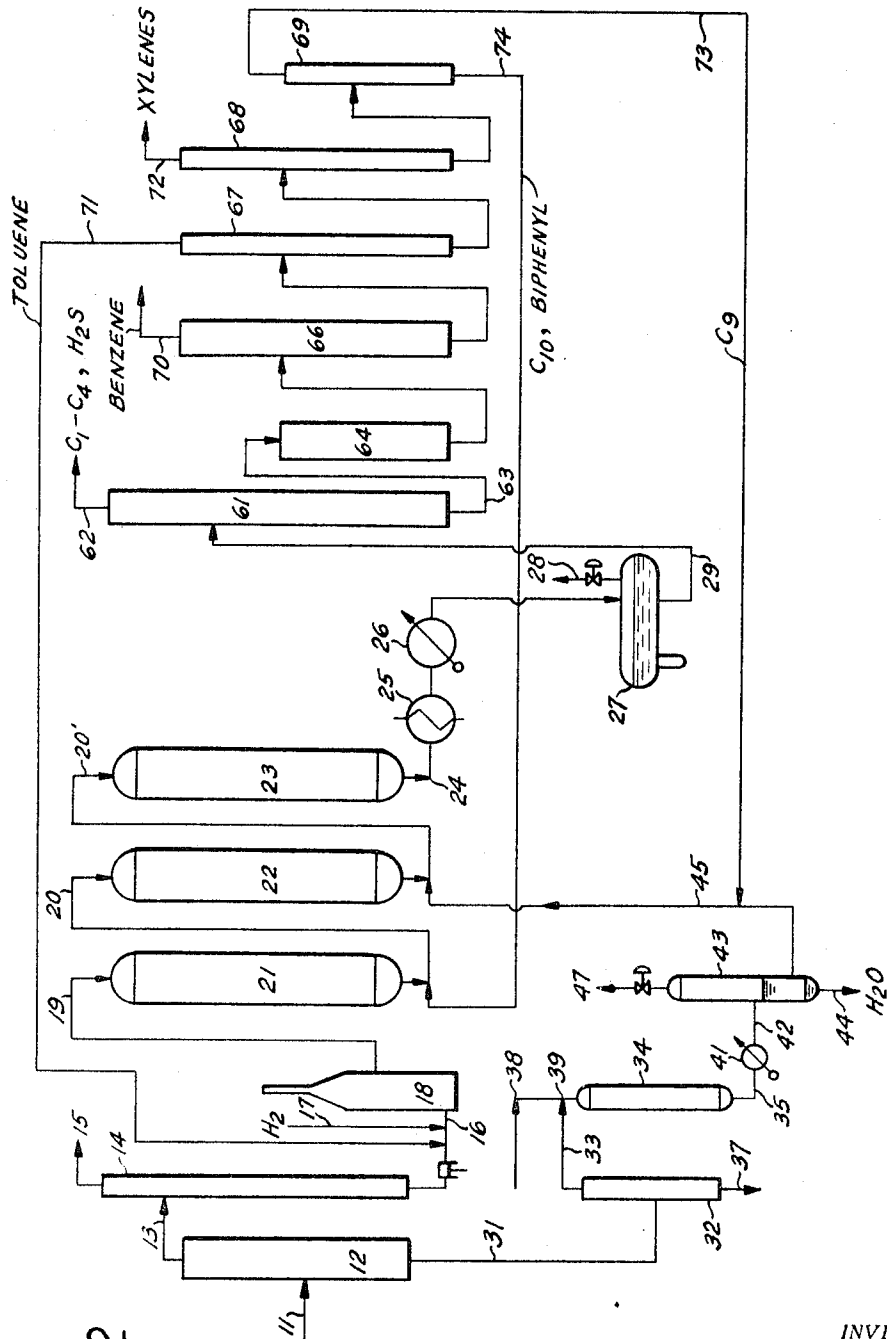


FIG. 2

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UPGRADING OF COKE OVEN LIGHT OILS

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Filed June 6, 1968, Ser. No. 735,131

Int. Cl. C07c 3/42, 3/58

U.S. Cl. 260—672

11 Claims

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ABSTRACT OF THE DISCLOSURE

In a process for upgrading an aromatic feedstock containing polymerizable impurities and oxygen compounds, the feedstock is fractionated into a benzene-toluene (BT) fraction boiling between 80° and 120° C., a fraction containing compounds having from 8 to 10 carbon atoms and boiling between 120° and 200° C., and, if present, into fractions boiling below 80° C. and above 200° C. The BT fraction is vaporized with hot hydrogen without polymer formation, further heated and hydrodealkylated in a hydro-upgrading zone in the presence of a chromia-alumina catalyst. The C₈ to C₁₀ fraction including the xylenes is vaporized and hydrotreated in the presence of a hydrotreating catalyst such as cobalt- or nickel-molybdate on alumina to a polymer-free and oxygen-free aromatic stream, and the thus treated fraction, free of water is further heated and refined by hydrodealkylating in the later stages of the hydro-upgrading zone. From both treated fractions a product is obtained comprising benzene, toluene and xylenes, and any non-converted C₉ and C₁₀ aromatics may be recycled.

Background of the invention

This invention relates to an improvement in the upgrading of aromatic hydrocarbons, and pertains particularly to the hydrogenation of crude light oil obtained by the carbonization of coal.

Crude light oils obtained during the carbonization of coal contain principally one-ring aromatics which are associated with numerous impurities. The aromatics include benzene, toluene, xylenes, ethylbenzene and trimethylbenzenes. The impurities include paraffins, naphthenes, olefins, carbon disulfide, phenol, heterocyclic compounds such as thiophenes, pyridines and coumarone, and certain unsaturated derivatives such as styrene and indene.

A method increasingly used to refine crude light oil is that by which crude feedstock is vaporized and treated with hydrogen, or hydrogen mixed with other gases, in the presence of a catalyst at elevated pressure and temperature. This type of treatment is known variously as hydrogenation, hydrodesulfurization, hydrodenitrogenation, hydrocracking, hydrofining or hydrodealkylation.

I prefer to refer to these processes, collectively, as "hydro-upgrading" processes, and wish to include in this definition any non-coal chemical refining process which treats one-ring aromatic hydrocarbons containing heat-polymerizable components.

In hydro-upgrading processes, impurities are converted into compounds which can be separated readily from benzene, toluene and xylene by subsequent operations such as condensation, stripping, fractional distillation, azeotropic distillation, solvent extraction or combinations

thereof. Hydro-upgrading processes are usually performed at temperatures which may range from 190° C. to 680° C.

In order to hydro-upgrade light oils, it is necessary to vaporize them. However, under pressure, and with increasing temperature, unsaturated compounds such as styrene, indene and coumarone, contained in light oils, tend to polymerize in the form of tarry compounds which are soluble in liquid phase in the aromatic feedstock. This solubility is unlimited. When the feedstock containing these polymers is exposed to a hot surface, such as that of a heat exchanger or heater, the polymer deposits on the hot surface and tends to build up in an increasingly thicker and harder layer, thus decreasing considerably the heat transfer to the feedstock, and requiring costly maintenance work in the operation of the heat exchanger, etc.

The polymerization reaction also occurs in vapor phase when the vapors of an aromatic feedstock containing polymerizable impurities are exposed to hot surfaces, resulting in the fouling of these surfaces.

In addition, polymerized impurities of the feedstock form excessive coke on many hydro-upgrading catalysts.

The rate of polymer formation is considerably greater in liquid phase or in mixed phase, than in dry gas phase.

Certain hydro-upgrading processes, described in the art, have considered the use of a preliminary catalytic reactor, usually referred to as a treater, pretreater or guard case, ahead of the main catalytic reactor in order to selectively convert polymer-formers to non-polymerizable compounds at a relatively low temperature. Following this preliminary treatment, the feed vapors can be heated with safety to the higher temperature of the main hydro-upgrading reactor.

Generally, in hydro-upgrading processes which use a pretreater, the total feedstock is pretreated and hydro-upgraded in one stream. Usually, the regeneration cycle of the pretreat catalyst is in the order of from one to two months, while some hydro-upgrading processes require regeneration of the catalyst about once a year. In either event, the entire upgrading system must be shut down during regeneration of the catalyst when the complete process is performed in a single stream. This practice reduces the overall capacity of an installation. It would, of course, be possible to use two parallel pretreat reactors, each capable of treating the total feed, and to regenerate the catalyst in one, while the other is on stream. However, such a system involves considerably higher capital expenditure, and therefore is not a desirable solution.

Certain hydro-upgrading processes, for example the Litol process, described in United States Patent No. 3,081,259, and in an article by M. O. Tarhan and L. H. Windsor in the February, 1966 issue of "Chemical Engineering Progress" at pages 67-72, cannot handle feedstocks containing appreciable amounts of oxygen compounds because the hydrogenation products contain water which is harmful to the alumina support of the catalyst. Consequently, a process of this type cannot upgrade the fraction of light oil which boils between 160° C. and 200° C., as this fraction contains a considerable amount of coumarone, as well as some phenol. In a process of the Litol type, coumarone and phenol would be deoxy-

generated, and the resultant water would affect the catalyst adversely. Thus, coumarone presents both the problem of gum formation and water formation.

In hydro-upgrading processes which dealkylate toluene and xylene to benzene, such as the Litol process referred to above, the conversion of all of the toluene to benzene is usually economically desirable, while dealkylation of the xylenes is usually undesirable. In the Litol process, at the relatively low liquid hourly space velocity (LHSV) used, there is approximately 90% conversion of the xylenes. It is thus economically desirable to treat the xylenes and higher boiling light oil fractions at a higher LHSV so that the xylenes are well-refined but with less dealkylation.

It is therefore an object of this invention to provide a method of converting polymerizable compounds contained in aromatic feedstock to non-polymerizable compounds.

It is another object to de-oxygenate oxygen-containing compounds prior to contact of the feedstock with water-sensitive hydro-upgrading catalysts.

A further object is to produce a refined aromatic product with a minimum of dealkylation of the xylenes, while maintaining a maximum of toluene dealkylation.

Summary of the invention

I have found that a light oil feedstock containing polymerizable compounds and oxygen-containing compounds can be refined most efficiently by separating the feedstock into two streams, one stream representing the low boiling fractions, and the other the higher boiling fractions which normally contain the polymer-formers and oxygen-containing compounds. This latter fraction will represent only a small percentage of the total feed. The low-boiling fraction, boiling below about 120° C., is vaporized in the presence of hydrogen and heated to the temperature required in the subsequent hydro-upgrading step, this portion of the feedstock then being fed to the hydro-upgrading zone comprising a first and second stage in series, where it is reacted in both stages in the presence of a chromia-alumina catalyst to hydrocrack olefins, paraffins and naphthalene to C₁ to C₄ aliphatics, to hydrogenate sulfur compounds such as thiophenes, and to hydro-dealkylate toluene to benzene.

The higher boiling fraction is sent to a pretreat reactor, where it is reacted with hydrogen in the presence of a hydrogenation catalyst. Here, polymer-formers are converted to non-polymerizable matter, and oxygen-containing compounds are converted to hydrocarbons and water. The effluent from the pretreater, after removal of water therefrom, is introduced into the second stage of the hydro-upgrading zone, where it is reacted to hydrocrack paraffins and naphthenes, to desulfurize sulfur compounds, and to hydro-dealkylate the C₉ and C₁₀ compounds. Some xylene is also dealkylated. The effluent of the hydro-upgrading zone is liquefied and separated from gases. Trace impurities are removed from the liquid product, and said product is fractionated to benzene, toluene and xylenes, and the residue containing any C₉ and C₁₀ compounds is recycled to the second stage of the hydro-upgrading zone.

Brief description of the drawings

In the accompanying drawings, FIGURE 1 is a schematic representation of a preferred mode of hydro-upgrading separate fractions of a crude light oil.

FIGURE 2 is a modification of FIGURE 1.

Detailed description

Referring to FIGURE 1, crude light oil, obtained from coal carbonization, enters rectification tower 12 by way of line 11. The oil is separated into two fractions, one fraction boiling above 120° C. and the other boiling below 120° C. The lower boiling fraction enters, by way of line 13, forerun removal still 14. Foreruns, making up the portion in the still boiling below 80° C., are removed overhead at line 15. This portion may be burned as waste

or disposed of in some other manner. The bottoms, boiling between 80° and 120° C. contain benzene, toluene, a certain amount of sulfur in the form of thiophenes, and non-aromatic impurities usually associated with this fraction. The bottoms are withdrawn from the still 14, mixed with hot hydrogen gas from line 17 at line 16, heated to approximately 600° C. in heater 18 and passed, by way of lines 19 and 20, to reactors 21 and 22 in series. Reactors 21 and 22 contain a fixed-bed of chromia-alumina catalyst. The feed in the reactors is maintained at a temperature between 600° and 640° C. and a pressure of about 800 to 840 p.s.i.g. A hydrogen to aromatics ratio of 4:1 to 7:1 is maintained. In the reactors, a certain amount of toluene is dealkylated to benzene, impurities in the form of aliphatic hydrocarbons are cracked to C₁ to C₄ aliphatic gases which are readily separable from the aromatic values of the feed, and thiophene is converted to readily separable hydrogen sulfide and C₁ to C₄ aliphatics. Gaseous effluent, withdrawn from second reactor 22, passes through line 24, heat exchanger 25 and cooler-condenser 26 to gas-liquid separator 27, where gaseous waste products comprising hydrogen sulfide, paraffins, and excess hydrogen are exhausted at line 28. Hydrogen is recovered from the exhaust gas and recycled in purified condition to the system. Liquid product, containing a mixture of benzene, toluene and, usually, as will be explained, xylenes, is withdrawn from separator 27 by way of line 29. Further refining steps, not shown, of this liquid product include further separation of small amounts of gaseous impurities in a stripping tower, clay treating to remove residual olefins, and fractionating to separate the purified product into its saleable components of benzene and toluene, and xylene if present.

Returning now to rectification tower 12, liquid bottoms are withdrawn from the tower at line 31. These bottoms represent the crude light oil boiling above 120° C., and they are introduced into fractionation tower 32, where that fraction boiling between 120° C. and 200° C. is led off overhead by way of line 33 to a pretreating reactor, or pretreater, 34. The residue from tower 32, comprising components of the crude light oil which boil above 200° C., such as naphthalene, is withdrawn at line 37. This residue may be utilized as fuel, or the naphthalene may be recovered.

Just prior to entering pretreater 34 the liquid feed from tower 32 is mixed, at 39, with hot hydrogen from line 38 bringing the incoming feed to a temperature of about 325° C. This mixing insures complete vaporization of the feed as it enters reactor 34. The feed contains a mixture of xylenes, ethyl benzene, trimethyl benzene and other alkyl benzenes. The feed also contains numerous alkylated thiophenes. More serious is the fact that the feed contains polymer-forming materials such as styrene, indene and coumarone. As has been explained, when styrene and the other polymer-formers are heated for an appreciable time, they tend to polymerize, resulting in the formation of gummy materials which settle out in heating units, heat exchangers, pipes, valves and the walls of reactor vessels. In a continuous process for the refining of crude light oil, the build-up of gummy deposits at critical points in the process equipment can be of such magnitude as to render the system practically inoperative until the gum deposits are removed. This results in an excessive amount of downtime and consequent economic loss.

This invention overcomes the formation of objectionable gummy material anywhere in the system by dividing the crude light oil stream at the rectification tower as described. The rectification tower must be designed to produce an overhead fraction which contains no gum-forming material. This fraction, boiling below 120° C., can therefore be sent to the main reactors 21 and 22 without pretreatment. The portion of the light oil boiling above 120° C. contains the gum-formers, and steps must be taken to eliminate gum formation therefrom. In addition, coumarone, along with any phenol present in the

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higher boiling crude light oil portion, contains oxygen. When oxygen-containing compounds are introduced into the hydro-upgrading reactors 21 and 22, water is produced in the reactor, and this has a deleterious effect on the chromia-alumina catalyst used in these reactors. In this invention, both the polymer-formers and the oxygen-containing compounds are rendered innocuous by hydrogenation in the pretreater 34 and a subsequent water elimination step.

In pretreater 34, which contains a fixed bed catalyst of pre-sulfided nickel-molybdate on alumina, vaporized feed is hydrogenated in the presence of the catalyst, and the polymerizable compounds are rendered non-polymer-forming. For example, styrene is converted to ethyl benzene, and indene to indan. Coumarone under these conditions is completely converted to ethyl benzene, ethyl cyclohexane and water, the water containing all of the oxygen from these compounds. The reactions are performed at a temperature of 350° C., a hydrogen-to-feed mol ratio of 5:1, a hydrogen partial pressure of 625 p.s.i.g., and at 2 LHSV. The treated feed, free of all polymer-forming components, but containing the converted forms of these components for further upgrading, is withdrawn from pretreater 34 as gaseous effluent at line 35. The effluent is cooled in cooler 41 to condense pretreated C₈ to C₁₀ vapors and the water vapor resulting from the reaction of the oxygen-containing compounds with hydrogen, and is transferred by line 42 to liquid-gas separator 43, where water is withdrawn at line 44. Excess hydrogen is exhausted at line 47 and sent to the hydrogen purification zone for recycling. The liquid effluent representing the treated feed is withdrawn from separator 43 and sent to the second in series of the hydro-upgrading reactors 22 by way of line 45. The effluent entering reactor 22 from separator 43 contains mostly C₈ to C₁₀ aromatics. This feed is mixed, in reactor 22, with treated feed from reactor 21, this latter feed now comprising principally benzene and a small amount of toluene. In reactor 22, the temperature is maintained in the range between 600° and 640° C. and at a pressure in the range of from 800 to 840 p.s.i.g.

Effluent from the pretreater, on entering the hydro-upgrading zone, may be utilized as a quench of the main stream to maintain proper temperature in the second stage of the hydro-upgrading zone.

By passing the pretreated stream of C₈ to C₁₀ aromatics through only the second of the two hydro-upgrading stages, the dealkylation of C₈ to C₁₀ aromatics is decreased substantially, while toluene which passes through both stages is dealkylated with a conversion of about 60%. Thus, the xylene retention is increased and the dealkylation of C₉ and C₁₀ aromatics is not permitted to proceed substantially beyond the C₈ level. Treatment of C₈ to C₁₀ aromatics in one hydro-upgrading stage only is sufficient to convert all of the residual sulfur and nitrogen compounds contained in the pretreated stream. Thus, by treating two light oil fractions at different space velocities in the hydro-upgrading zone all of the impurities will be converted to forms readily separable from the aromatic product, while at the same time high yields of economically important benzene and xylenes can be obtained. The treated feed is withdrawn from reactor 22 as gaseous effluent by way of line 24 to heat exchanger 25 and cooler 26, thence to liquid-gas separator 27. Paraffinic gases and hydrogen sulfide resulting from the refining process in reactors 21 and 22 and hydrogen are exhausted from separator 27 by way of line 28, the hydrogen being subsequently purified and returned to the system. Liquid product, withdrawn at line 29, is further refined in a series of steps, not shown, which include sending the product to a stripping tower for further separation of gases from the product, to a clay treater for removal of residual olefins and then to a fractionator, where the refined aromatic product is separated into benzene, toluene and xylene, and residual

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C₉ and C₁₀ aromatics. The residuals are recycled to the second hydro-upgrading stage.

Under the conditions present in the hydro-upgrading zone, pyridines are hydrogenated to nitrogen-free aliphatic compounds which are readily separated from benzene.

The separation of crude light oil into the desired fractions can be performed in any manner known in the art, provided the fractionation is sufficiently effective to leave no polymer formers in the lower-boiling fraction (80°–120° C.) and polymer formation is avoided by not allowing the feedstock extended residence time at elevated temperature anywhere in the fractionation system. It is preferable to use an overhead product for the 120°–200° C. fraction and to process this fraction without delay in the pretreater.

It is preferable to vaporize the 120°–200° C. fraction by blending the unpreheated feedstock with hot hydrogen prior to the inlet to the pretreat reactor. It is also preferable to vaporize this fraction by blending the unpreheated feedstock with the hot hydrogen in a pipe-T, in order to speed up the vaporization to a dry vapor. However, these operations may be performed by alternate means known to the art, provided such means does not lead to polymer formation.

The temperature in the pretreater may range from about 250° to 375° C., preferably 300° to 350° C., and the pressure should be maintained between 300 and 1500 p.s.i.g. The LHSV may be within the range of 0.5 to 4.0, and preferably between from 1 to 2. Hydrogen to aromatics mol ratio may range between 2.5:1 and 10:1.

A presulfided nickel-molybdate on alumina catalyst has been found to be the most satisfactory catalyst for use in the pretreater for converting polymerizable components to a non-polymerizable form and for de-oxygenating the oxygen-containing compounds. However, other catalysts have been used which give a satisfactory performance, chief of which is presulfided cobalt-molybdate on alumina.

The temperature and pressure in the hydro-upgrading reactors may range from 550° C. to 675° C. and from 500 to 1500 p.s.i.g. respectively. The preferred temperature range is from 600° to 640° C.

In the preferred example, a hydro-upgrading zone is used comprising two stages, each stage represented by a reactor. However, according to the purity requirements of various product markets, the relative severities of each hydro-upgrading stage, in terms of residence times, may be varied as desired, provided the pretreated C₈ to C₁₀ stream can be sufficiently refined. Also, more than two stages may be used. It may also be desirable to separate fractionally various fractions of residual C₈, C₉ and C₁₀ aromatics, and to subject them to selected hydro-upgrading severities by recycling said fractions to the proper hydro-upgrading stages, so that most of the C₉ and C₁₀ aromatics are converted to xylenes, and a minimum of xylenes are converted to toluene and benzene.

If the selected fraction to the pretreater contains components boiling below 160° C. only, thus excluding the oxygen-containing compounds, the condenser and liquid-gas separator following the pretreater may be omitted.

While the feedstock in the example is a crude light oil from coke manufacture, the invention can be applied to other aromatic feedstock containing styrene, indene, coumarone, conjugated diolefins such as cyclopentadienes and/or phenol.

In order to more clearly delineate the components of the crude light oil fractions discussed in this invention, a table is given below in which light oil is characterized broadly by its well-known commercially treated fractions, i.e. forerunnings, secondary light oil and primary light oil. These fractions are further identified by the more important values, as well as certain recognized impurities, contained therein. Boiling points of individual components are shown in degrees centigrade.

	Aromatic Compounds	Unsaturated Gum-formers and Oxygenated Compounds	Sulfur Compounds	Nitrogen Compounds	Selected Fraction
Forerunnings.....		Cyclopentadiene 42°	Carbon bisulfide, mercaptans, hydrogen sulfide, etc. to 46.3°		1, discarded.
Secondary Light Oil.....	Benzene 80°, toluene 110° o, m and p xylenes 133°-144°, ethyl benzene 136°	Styrene 145°	Thiophene 84°, 2 and 3 methyl thiophenes 113°-115° Other methyl thiophenes 136°-146°	Pyridene 115°	2, to hydro-upgrading reactor.
Primary Light Oil.....	Propyl benzene 159°, polyalkyl benzenes and toluenes 153°-177° Naphthalene 218°	Dicyclopentadiene 170°, coumarone 174°, indenes 182°-198°, phenol 182°	Other methyl thiophenes 163°-180°	Methyl and ethyl pyridenes 129°-195°	3, to pretreater then to hydro-upgrading reactor.
					4, recovered, or burned as fuel.

The foregoing table is not intended as an exhaustive listing of the components found in light oil, there being other components present in minor quantities, and which have no significant effect on the process, which have not been included.

Dividing the feedstock into two streams, as has been described in the foregoing example, and introducing the higher boiling stream into the pretreater as shown, provides the several advantages of preventing formation of any gummy residue in the system, use of a small pretreater to handle only that fraction which contains gum-formers and oxygen-containing compounds (less than 6% of the total feed) and permitting refining operations to proceed on the benzene-toluene fraction (selected fraction 2 of table) while the pretreater catalyst is being regenerated.

While the process of this invention is designed as a continuous operation, storage tanks may be supplied as temporary reservoirs in order to accumulate the C₈ to C₁₀ fraction during the start-ups and catalyst regeneration of the pretreating and of the hydro-upgrading unit. In fact, it is an economic advantage that the hydro-upgrading unit can continue operation during the shutdown of the pretreater and presulfiding and regeneration of the pretreated catalyst.

A modification of the process of FIGURE 1 is shown in FIGURE 2, wherein the hydro-upgrading zone consists of three stages, or reactors, to provide greater flexibility in hydrodealkylating C₉-C₁₀ aromatics selectively to the C₈ level.

The separation of crude light oil into an 80°-120° C. fraction and a 120°-200° C. fraction, and the pretreating of the 120°-200° C. fraction, are performed exactly as described in the previous example.

Referring to FIGURE 2, the lower-boiling 80°-120° C. fraction, containing mainly benzene and toluene, is withdrawn from forerun removal still 14, and mixed with hot hydrogen gas from line 17 at line 16. This portion of the feed is heated to approximately 600° C. in heater 18, and passed, by way of lines 19, 20 and 20' to reactors 21, 22 and 23 respectively, in series. Reactors 21, 22 and 23 each contain a fixed bed of chromia-alumina catalyst, and they operate under the same conditions as described in the previous example, except that the total amount of catalyst is distributed throughout a total of three reactors instead of two. Gaseous effluent, withdrawn from last reactor 23, passes through heat exchanger 25 and cooler-condenser 26 to gas-liquid separator 27. In separator 27, the condensed liquid product still retains some hydrogen, hydrogen sulfide and C₁-C₄ hydrocarbons in dissolved state, corresponding to the absorption equilibria of these gases between gas and liquid phases at the temperature and pressure existing in the liquid-gas separator. These dissolved gases are stripped from the liquid product in a stripper 61. The bottoms from the stripper are sent through line 63 to a clay treater 64, and through successive fractionation columns 66, 67, 68 and 69. Waste gas, containing hydrogen sulfide and C₁-C₄ aliphatics, is exhausted overhead from stripper 61 at line 62. The products removed overhead from columns 66 through 69 are pure benzene, pure toluene, pure mixed xylenes and refined C₉ aromatics, and

are withdrawn at lines 70, 71, 72 and 73 respectively. Toluene is recycled to the crude 80°-120° C. feed fraction for total conversion to benzene. The two products of the process are pure benzene and a purified mixture of C₈ aromatics comprising xylene isomers and ethylbenzene. The refined C₉ fraction is recycled to the inlet of reactor 23. The bottom fraction of column 69 contains mainly C₁₀ aromatics and biphenyl, the latter being formed in reactors 21, 22 and 23 as a byproduct of hydro-dealkylation. This bottom fraction from still 69 is recycled to the inlet of reactor 22, by way of line 74, for further dealkylation. The presence of recycled biphenyl suppresses formation of additional biphenyl in reactors 22 and 23.

By recycling C₉ and C₁₀ fractions to different reactors, these fractions are hydro-dealkylated, each to a different degree, so that both fractions are converted substantially to C₈ aromatics.

In this example, only three reactors, or stages are used. Optionally, a greater number of stages may be used, as well as stages which contain different amounts of catalyst. It is not required that the different stages be employed in the form of separate reactors as shown. One or two reactors may be used, with injection of the recycle streams into locations at points on the reactors which have been calculated to give the optimum conversion to C₈ aromatics.

The fractionation of the hydro-upgrading product is performed in this example in four continuous columns, however, the same fractionation can be performed by any other method known to the art, provided the products of fractionation are of the desired purity.

In this invention, polymerizable components and oxygen-containing compounds contained in aromatic feedstocks boiling up to 200° C. are quantitatively converted into non-polymerizable and oxygen-free compounds, and are recovered as saleable products, such as benzene, toluene, xylene, and ethylbenzene. Aromatic feedstocks containing oxygen-containing compounds, such as coumarone and phenol, are rendered usable in light oil refining processes with a water-sensitive chromia-alumina catalyst. Due to the treatment of the lower boiling fraction in the entire hydro-upgrading zone, maximum conversion of toluene to benzene is maintained, while at the same time conversion of the C₈-C₁₀ fraction below the C₈ level is effectively decreased. In addition, any unconverted C₉ and C₁₀ aromatics can be fractionally separated and recycled to the proper hydro-upgrading stages. The pretreatment of the polymerizable compounds and oxygen-containing compounds in a small side stream, independent from the main process stream, improves the economics, safety and operating convenience of a light oil hydro-upgrading process which both refines and hydro-dealkylates.

I claim:

1. A method of upgrading aromatic feedstock boiling up to 200° C. and containing polymerizable compounds, oxygen-containing compounds, non-aromatics and sulfur compounds which comprises separating said feedstock into a first fraction boiling between 80° C. and 120° C. and a second fraction boiling between 120° C. and 200° C., vaporizing and heating said first fraction to the reaction temperature of a hydro-upgrading zone and introducing the fraction into the first and subsequent stage or stages

of a hydro-upgrading zone and therein reacting said first fraction with hydrogen in the presence of a chromia-alumina catalyst at a temperature between 550° C. and 675° C. and a pressure between 400 and 1500 p.s.i.g., introduced during said second fraction, free of polymerized material, into a pretreating zone and therein reacting the fraction with hydrogen in the presence of a hydrogenation catalyst at a temperature between 250° C. and 375° C., and a pressure between 400 and 1500 p.s.i.g. at a liquid hourly space velocity of 0.5 to 4 vol./ (vol.) (hr.) and thereby converting polymerizable compounds to non-polymerizable compounds and oxygen-containing compounds to non-oxygen-containing compounds, removing the thus-treated fraction from the pretreating zone, supplying said treated fraction in a water-free condition to the second or subsequent stages of the hydro-upgrading zone, and withdrawing the treated fractions as effluent from the hydro-upgrading zone.

2. A method according to claim 1 in which the hydrogenation catalyst in the pretreating zone is nickel-molybdate on alumina.

3. A method according to claim 1 in which the hydrogenation catalyst in the pretreating zone is cobalt-molybdate on alumina.

4. A method according to claim 1 wherein the second fraction is introduced into the pretreating zone in unpreheated liquid phase.

5. A method according to claim 1 wherein the hydro-upgrading is divided into two stages, the low-boiling fraction only being treated in the first stage and a mixture of first stage effluent and pretreated C₈-C₁₀ effluent is treated in the second stage.

6. A method according to claim 1 wherein the treated fraction from the pretreating zone is cooled and condensed to a point where substantially all the water is liquefied and said water is separated from the remaining treated fraction.

7. A method according to claim 1 in which the aromatic feedstock is a light oil obtained from the carbonization of coal.

8. A method according to claim 1 in which a hydrogen to aromatics mol ratio is maintained in the hydro-upgrading zone at between 4:1 and 7:1 and in the pretreating zone at between 2.5:1 to 10:1.

9. A method according to claim 1 wherein the hydro-upgrading zone has more than two stages with the low-boiling fraction only being treated in the first stage.

10. A method according to claim 9 in which the effluent from the hydro-upgrading zone is condensed, separated from gases and fractionally separated into pure benzene, toluene, xylenes and several C₉-C₁₀ fractions, the C₉-C₁₀ fractions being recycled to selected upgrading stages subsequent to the first stage for conversion to xylenes.

11. A method according to claim 1 wherein the temperature in the hydro-upgrading zone is between 600° and 640° C.

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G. E. SCHMITKONS, *Assistant Examiner.*

U.S. Cl. X.R.

208—48, 57, 78, 80, 210, 211, 213; 260—674

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,449,460

June 10, 1969

Mehmet Orhan Tarhan

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 53, "sensitive" should read -- sensitive --.
Column 9, line 5, "introduced during" should read --
introducing --.

Signed and sealed this 17th day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents