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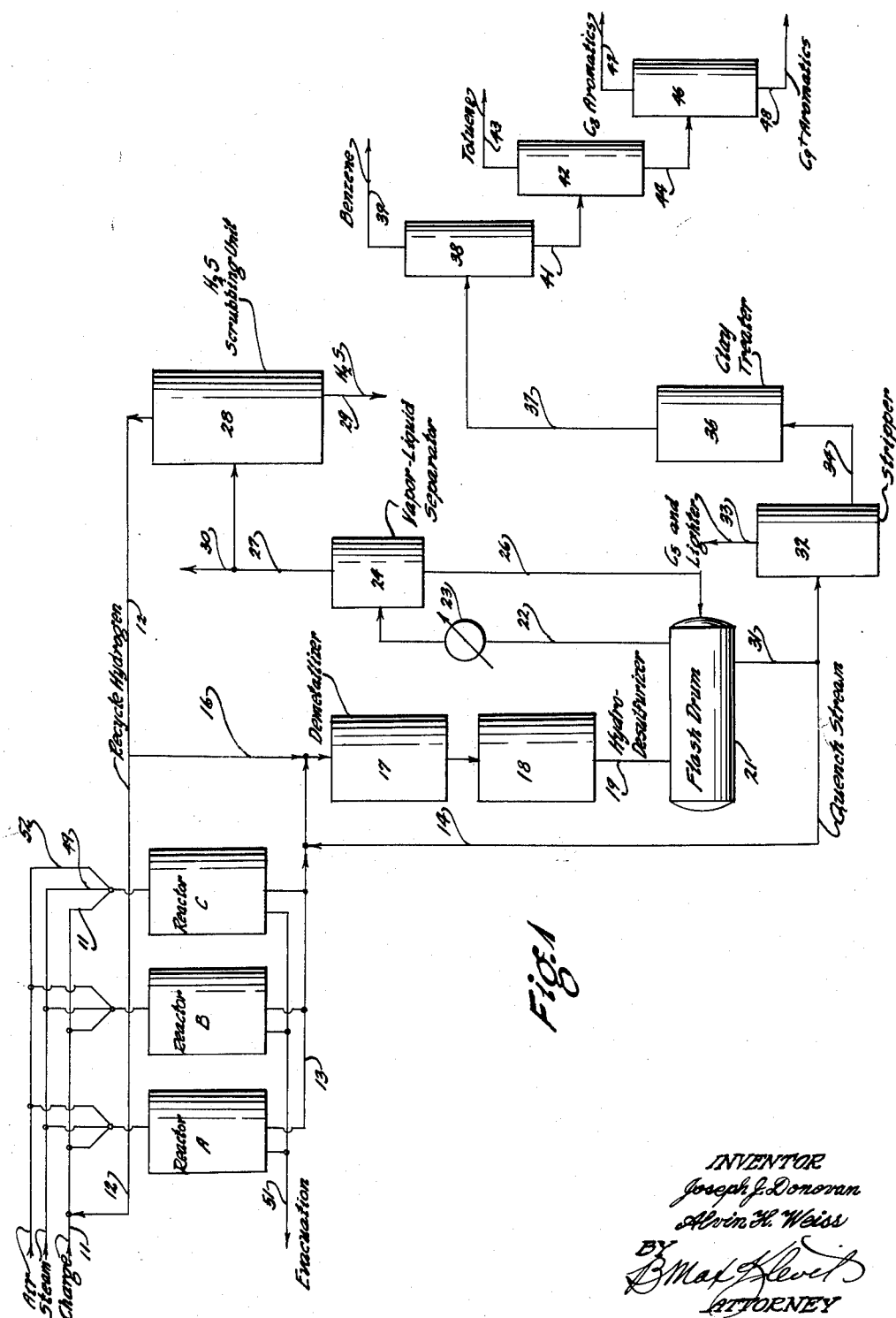
J. J. DONOVAN ETAL

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COKE OVEN LIGHT OIL PURIFICATION

Filed Aug. 18, 1959

2 Sheets-Sheet 1



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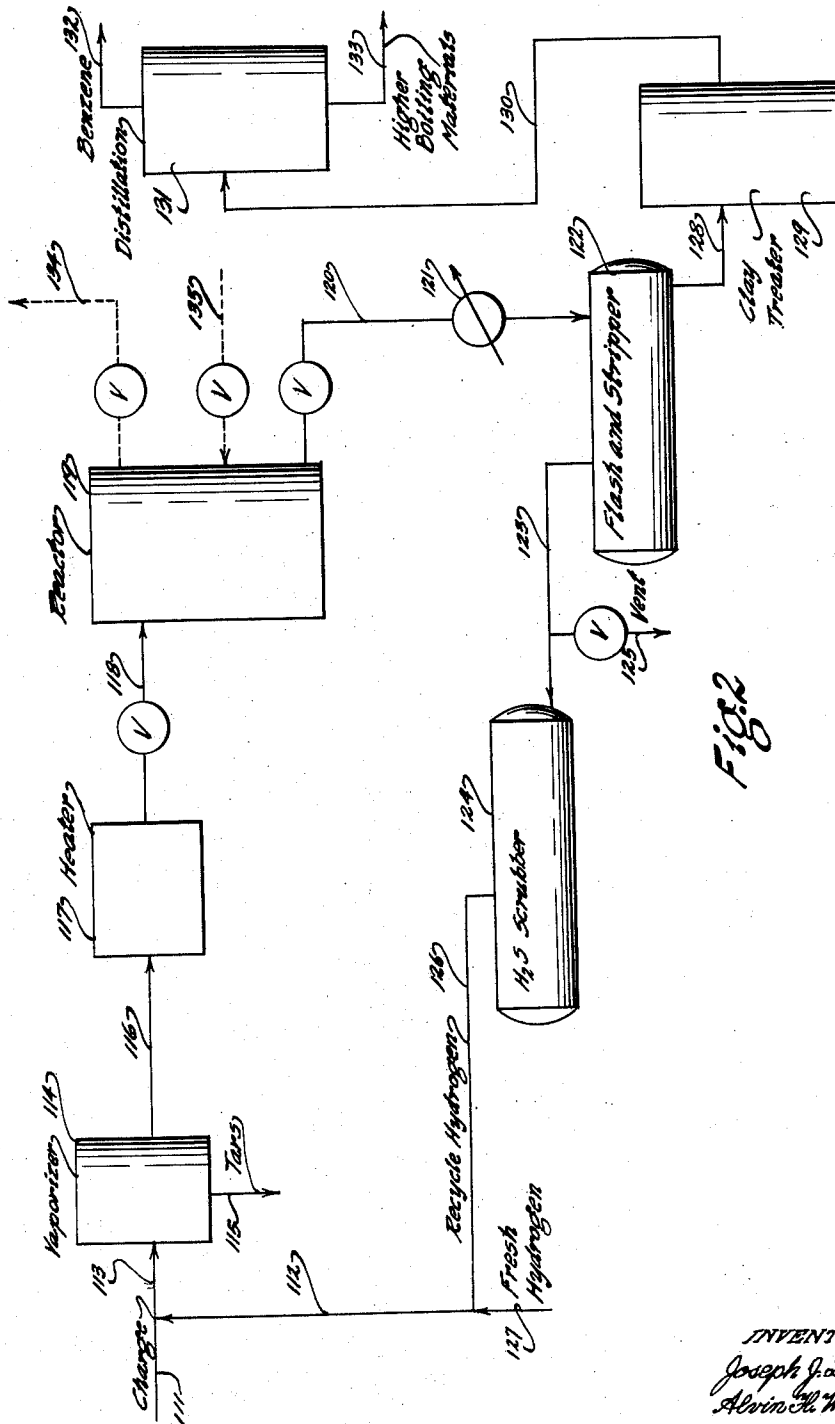


Fig. 2

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3,081,259

COKE OVEN LIGHT OIL PURIFICATION

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13 Claims. (Cl. 208-216)

This invention is concerned with the purification of coke oven light oil to obtain therefrom substantially pure aromatics.

The light oils produced as by-products in coke oven plants contain benzene and benzene-type hydrocarbons in relatively high proportions; however, these light oils are contaminated with a wide variety of hydrocarbonaceous materials such as those that are paraffinic or unsaturated or naphthenic in nature as well as up to sizeable quantities of sulfur-containing compounds. The aromatics being of higher value are preferably recovered in high yield and in high purity in order to realize the full value thereof. Removal of the several extraneous contaminants is a problem of long standing and one for which a wide variety of processes have been suggested. Some of these processes have been utilized with greater or less success in the separation and recovery of purified aromatic portions of coke oven light oil.

Inasmuch as coals differ in their coking characteristics and in the by-product materials recovered from such coking operations, the nature of the coke oven light oil varies rather widely and no exact listing of all of the impurities in all of the oils is available. Likewise unavailable is the quantity of such impurities to be expected except as determined for an individual batch of such oils. In general the types of impurities fall into the classes of hydrocarbonaceous materials boiling in the range of about 40° C. to about 150° C., such as cyclopentanes, cyclohexanes, cyclo-olefins, normal and branched chain paraffins and olefins, and aromatic olefins; arsenic; and organic sulfur compounds of which thiophenes are in appreciable quantity and are one of the more objectionable impurities in being persistent and resistant to ready separation.

As noted above the aromatic portions of the light oils are commercially valuable when freed of the extraneous materials. Such purified aromatics are of decided value in the preparation of various pharmaceuticals and dye stuffs; whereas the presence of contaminating materials is a threat to the desired reactions and may well introduce catalyst poisons or catalytic effects in manufacturing processes which are detrimental. Even the relatively moderate requirements with respect to nitration grade toluene have on occasion been hard to achieve because of the difficulty of removal of paraffinic-type hydrocarbons; even so industry has listed some specifications in many instances considerably more rigorous than required for nitration grade toluene.

Of the many suggested processes a few have been employed to obtain the various aromatics with some, however, meeting the relatively rigid specifications only with relatively large losses of potentially valuable components because of the severity required in removing the more refractory impurities. Others obtain the high purity aromatics through multiple processing steps such as catalytic treatment followed by solvent extraction, or super-fractionation or combinations thereof in addition to the usual clay treatment for final "clean-up" of the product. It has now been found that high purity aromatics in excellent yields can be recovered from coke oven light oils by considerably simplified process.

In our parent application, Serial No. 788,872, filed January 26, 1959, of which the present application is a continuation in part, an improved method of obtaining aromatics

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from coke oven light oils is described. Claims allowed in said parent application were transferred hereto and said application abandoned. In said parent application, the preheated and vaporized light oil is subjected to multi-stage treatment wherein it is first contacted with a dehydrogenation catalyst resistant to sulfur poisoning in the presence of added H₂, and the resulting effluent is then subjected to hydrodesulfurization over a catalyst comprising a group VIII metal, preferably with an intervening absorptive treatment for removal of arsenic and heavy metals. The desulfurized product is given a final treatment over an adsorptive clay or other contact material for removal of any small amounts of olefins. The aforesaid application gives as conditions for the initial contact with dehydrogenation catalyst inlet temperature of 700° to about 1100° F., liquid hourly space velocities in the range of 0.2 to 2.0 v./hr./v., pressures of from below atmospheric up to 40 atmospheres (preferably 3 to 10 atmospheres) and H₂ addition at the rate of 0 to 4.0 mols/mol light oil. The referred operation is 750° to 800° F. inlet temperature, 1200° to 1250° F. max. at outlet, 0.5 LHSV, 7 min. on-stream time, and 9 atmospheres pressure. While the product of this initial treatment is mainly aromatic it still has a relatively high sulfur content such as in the order of about 500 to 1000 p.p.m. and a bromine index of about 20 to 120; which necessitates the further purification advocated in the aforesaid application.

It has now been found that effective purification of coke oven light oil can be obtained in a single stage hydrodesulfurization operation if treatment of the oil is carried out at pressures within and above the high part of the preferred range described in the previous application, more specifically at pressures of no less than 400 pounds per square inch gauge (p.s.i.g.) and up to 1000 p.s.i.g. and at a carefully controlled temperature lying in the range of 1110° to 1170° F. For successful operation of the one-step process it is important that the ratio of total hydrogen-containing gas be maintained within narrow limits of 3.1 to 6.3 mols per mol of fresh oil charged and that such gas include enough free hydrogen to maintain a minimum hydrogen partial pressure of no less than ½ the total pressure in the reactor; the space rates must be kept low so that the nominal residence time of the light oil in the reactor is not less than 60 seconds. Deviation in significant degree from these conditions results either in excessive coking or reduced purity of product or both. Moreover, the catalyst employed must be one of low coking characteristics. Such catalyst is obtained by compositing 5 to 40% Cr₂O₃ on alumina, by impregnation on a high area alumina base and subsequently surface-area adjusted by heat treatment to no less than 50 square meters per gram (m.²/g.).

While as a general rule the one-step procedure for purification of light oils is preferred, there are situations in which the multi-stage operation might be desirable despite its greater complexity and higher cost. In this connection it should be borne in mind that the one-step process will generally be operated at a higher pressure and requires more critical control of operating conditions; furthermore, it involves a higher requirement of hydrogen, which may be less available in certain localities. In the one-stage process, also, a significant portion of the C₇ and higher aromatics are dealkylated to benzene, so that if the preservation of the toluenes and xylenes in the ultimate product is desired, the multi-stage process may be the choice.

The operation of the multi-stage process is illustrated in FIG. 1 by a diagrammatic flow sheet, while that of the one-step method is similarly illustrated in FIG. 2.

EXAMPLE I

Referring to FIG. 1 a process is shown in which 2885 gallons per hour of coke oven light oil is to be treated. The oil has the following composition:

C ₆ , C ₇ , C ₈ and C ₉ benzenes	92.1 volume percent.
Hydrocarbon impurities	6.8 volume percent.
Thiophenes	1.1 volume percent.
Arsenic	150-200 parts per billion.
Bromine index	10,800.

The charge is introduced through line 11 at a temperature of 800° F. Hydrogen in an amount of one mol per mol of charge is simultaneously introduced through line 12. The charge plus hydrogen passes through reactor A for 7 minutes in contact with commercial chromia-alumina catalyst (20% chromia, 80% alumina) at conditions including a bed inlet temperature of about 800° F. Pressure is maintained at 130 p.s.i.g. and the liquid hourly space velocity is 0.5.

Product from reactor A passes through line 13 and is adjusted in temperature to 800° F. by introduction of a minor portion of recycle aromatics introduced through line 14 and recycle hydrogen introduced through line 16 to bring the hydrogen to oil ratio to 5:1, and the whole is passed to demetallizer zone 17 operated at 800° F. and approximately 110 p.s.i.g. Vessel 17 contains a cobalt molybdena on alumina catalyst in sulfided condition and is operated at 6 LHSV. The main reaction in reactor 17 is that of the removal of arsenic and heavy metals; however, some other reactions possibly occur.

The entire effluent without further temperature or pressure adjustment is passed through the hydrodesulfurization zone 18, at a space rate of 3 LHSV wherein the residual amounts of organic sulfur compounds are decomposed to products including H₂S. The effluent therefrom after suitable temperature adjustment is introduced through line 19 to flash drum 21 wherein an initial separation of vapor from liquid is effected. The flash drum is operated at about 100 p.s.i.g. (substantially the outlet pressure from hydrodesulfurization zone 18). The vapor effluent from drum 21 passes through line 22 and cooler 23 to further vapor-liquid separation zone 24. Liquid from zone 24 is returned through line 26 to flash drum 21 and liquid-free vapor is passed through line 27 to the H₂S scrubbing unit 28 wherein H₂S is selectively removed through line 29 and H₂-containing recycle gas is compressed by means not shown and passed through line 12 for recycle purposes as may be desired. Any excess gas produced in the process may be vented through line 30.

The liquid portion from flash drum 21 is withdrawn through line 31 and passed, with the exception of such minor portions as may go through line 14 for quench purposes, to a stripping zone 32 wherein C₈ and lighter products along with any water in the product stream are withdrawn through line 33. Approximately 2,731 gallons per hour of product material enters the stripper and 2,673 gallons per hour of liquid product, pressurized to 160 p.s.i.g. and temperature adjusted to 375° F. by means not shown, is passed through line 34 to clay treating zone 36 for removal of trace quantities of olefinic types of hydrocarbonaceous materials. From the clay treater, the effluent passes through line 37 to benzene fractionation tower 38 for substantially complete separation of the benzene which is removed through line 39. The bottoms from tower 38 pass through line 41 to the toluene fractionation tower 42. Substantially pure toluene is removed through line 43 and the bottoms from tower 42 pass through line 44 to the xylene fractionation tower 46 wherein complete separation of the C₈ benzenes from the C₉ and heavier fraction is effected. Pure C₈ aromatics are removed through line 47. C₉ and heavier aromatic bottoms are removed from tower 46 through line 48 and can be further fractionated to recover selected portions if so desired. The yields volumetrically are approximately 1,799 gallons per hour of benzene, 644 gallons per

hour of toluene, 182.5 gallons of C₈ aromatics, and 27.5 gallons per hour C₉₊ aromatics.

The first section of the reactor system operates on a cyclic basis on which reactors A, B and C are periodically on stream and being regenerated with intervening adjustment of conditions to permit regeneration and reaction. While reactor A is on-stream as indicated above, reactor B is first purged with steam through line 49 and then evacuated through line 51 to remove residual traces of hydrocarbonaceous materials. At the end of the purge and evacuation period, air is introduced through line 52 and is continued for approximately 7 minutes. Reactor B is evacuated and hydrogen purged and is then ready for admission of fresh charge through line 11. The same type of operating cycle occurs in reactor C. The cycle arrangement of the 3 reactors is so arranged that one reactor is on-stream with another reactor always ready to go on-stream with freshly regenerated catalyst upon completion of the on-stream portion of the cycle in one reactor, while the third reactor is concluding the steps of regeneration and/or preparation for reception of fresh charge.

The process has been described in some detail but is not necessarily limited to exact adherence to the steps described above; for example, while recycle hydrogen is the sole source of hydrogen shown in FIG. 1, required hydrogen may be introduced to the reactor from some extraneous source not shown. Quench stream utilization of a portion of the product stream may be suitably substituted by other means of temperature adjustment, such as indirect heat exchange. In other places, well-known and usual temperature and pressure adjustments may be suitably obtained by well known means inasmuch as these items form no part of the invention except as employed and used in the overall system. Clay treatment has been shown in treating zone 36; however, other means of removing olefinic hydrocarbons or such polymerizable materials as may be present can be satisfactorily substituted, as by acidic treatment other than the acid type clay-treating clay.

In general, the treatment in vessel 17 of the effluent product discharged from reactors A, B, and C through line 13, for removal of arsenic and other heavy metals, is carried out over a porous contact agent effective in the removal of arsenic and heavy metals at conditions of temperature in the range of 725° to 950° F., a liquid hourly space velocity in the range of 1 to about 25 volumes of oil (as liquid) per volume of contact agent, with added hydrogen in the range of 2 to 10 mols/mol of charge and at superatmospheric pressures with hydrocarbon partial pressures in the range of 0.4 to about 10 atmospheres; the product from the demetallizing treatment thereafter being passed over a hydrodesulfurizing catalyst containing a metal of group VIII of the periodic system and at conditions generally similar to that of the demetallizing treatment. The effluent from desulfurization is freed of gaseous products, adjusted to a temperature in the range of 300° to 375° F. and passed at a liquid hourly space velocity in the order of 1 to 6 and at a pressure in the range of 10 to 50 atmospheres over an adsorptive clay or suitable contact agent for the selective removal of any remaining traces of olefins.

Operation is accordance with this procedure, for example, gives a benzene in which the thiophene content is less than 1 part in a million; a freezing point of 5.4° C., corrected to dry basis according to ASTM procedure, or higher; and a bromine index (milligrams of bromine reacting with one hundred grams of sample) of less than 5. It is further to be noted that aromatics originally present in the charge are recovered in yields of at least 95% and usually in the order of 99% or better, which is a demonstration of a highly efficient and effective purification of a charge material long constituting a difficult purification problem.

With respect to the first catalytic treatment in the multi-

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stage process, it may be effected in the presence of a moving or a fixed bed of the proper type of catalyst. A particularly effective system is that in which adiabatic cyclic operation is effected using a fixed bed of catalyst. As a typical embodiment, light oil preheated to approximately 750° F. is passed at a liquid hourly space velocity of 0.5 into contact with hydrogen-treated chromia alumina catalyst, comprising 20% chromia supported on alumina, for a period of about 7 minutes with the bed inlet temperature maintained at about 750° F.

During this reaction the pressure is maintained at about 9 atmospheres. At the end of the period of charge oil introduction the catalyst is reactivated, which may be effected by steps which include a hydrogen purge followed by an evacuation with subsequent introduction of air for approximately 7 minutes to effect oxidative removal of the hydrocarbonaceous deposit and temperature adjustment. The temperature in the bed of catalyst increases in the direction of flow of the regeneration medium and is generally highest near the outlet. The temperature is not allowed to rise above about 1250° F. at any part of the bed in order that thermal deactivation of the catalyst does not result. After the period of regeneration there is a period of evacuation followed by a reduction treatment with added hydrogen and thereafter, in the presence or absence of added hydrogen, introduction of fresh amounts of the light oil charge. The light oil charge flows in the same direction as that of the regeneration medium and thus flows from the relatively cooler inlet portion of the bed through to the relatively warmer bed outlet. During the light oil on-stream period the bed inlet temperature is maintained above 700° F., such as about 750° to 800° F., and the maximum temperature, as at the bed outlet, is maintained in the order of 1200° to 1250° F.

The normally liquid portion of the product effluent from this catalytic treatment stage is mainly aromatics but still has a relatively high sulfur content such as in the order of up to about 500 to 1000 parts per million and a bromine index in the order of about 20 to 120, and may contain in the order of 10 to 30 parts per billion (p.p.b.) of arsenic. As previously indicated, this product is thereafter treated, with intervening removal of arsenic as may be required, to substantially completely remove sulfur compounds by passage at somewhat high space rate and an operating pressure of about 9 atmospheres and at a temperature in the range of about 725° to 950° F., preferably less than 900° F., over a hydrodesulfurizing catalyst, for example, metallic nickel supported on alumina or sulfided cobalt-molybdena supported on alumina catalyst, or other gasoline reforming type catalyst, preferably one comprising a group VIII noble metal, such as platinum, on alumina. Such treatment effects substantially complete conversion of free and combined sulfur to H₂S which is thereafter separated leaving normally liquid product relatively completely free of sulfur, but which may still contain trace quantities of olefinic hydrocarbons.

Effective reduction of the unsaturated hydrocarbons of the normally liquid product is obtained by selective adsorption of the unsaturates on an inorganic adsorptive mass such as the typical "clay treatment" clay, bauxite, fuller's earth, bentonites, synthetic silica-aluminas, silica-magnesia and the like, enabling the recovery of high yields of high purity aromatics.

Such clays as the commercially available "Filtrol" or "Attapulugus" or Edgar kaolin constitute a suitable adsorptive material whereby highly effective and substantially complete removal of unsaturates from the normally liquid components of the product effluent from the preceding desulfurization stage are obtained. As previously mentioned the operating conditions include liquid hourly space velocity in the order of 1 to 6 at a temperature of 300° to 375° F. and a pressure in the range of 10 to 30 atmospheres.

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With the usually available and typical light oil charge from coke oven by-product recovery, this process permits a purified liquid product recovery in the order of 80% or better of the original charge and such purified liquid constitutes 95% or better of the aromatics originally present in such charge.

Another typical operation in accordance with the multi-stage process is illustrated in the following example:

EXAMPLE II

A typical light oil charge identified below was passed over a commercially available dehydrogenation catalyst, comprising approximately 20% chromia supported on a high area activated alumina, after being preheated to 750° F. During the cyclic operation the bed inlet temperature was maintained at substantially 750° F. for the duration of the run. The bed outlet temperature was between 1200° F. and 1250° F. The light oil charge was introduced at a liquid hourly space velocity of 0.5 and a reaction pressure of 30 p.s.i.g.

Light Oil Charge

Boiling range, ° C.	About 60 to about 150.
Sulfur, wt. percent	0.75.
Composition, vol. percent:	
Benzene	66.8.
Toluene	21.5.
C ₈ aromatics	6.2.
C ₉ aromatics	0.6.
Styrenes and indene	2.0.
Thiophenes	1.0.
Paraffins	1.0.
Olefins	0.9.

The effluent from the first reaction zone, containing better than 90% by weight of the charge of normally liquid components, was thereafter freed of arsenic and further desulfurized over a catalyst comprising 25% by weight of metallic nickel supported on activated alumina. The temperature was held in the range of 675° to 700° F., the space rate was 3 (volumes of charge as liquid per volume of catalyst per hour) and the pressure conditions were held at 30 p.s.i.g. The effluent from this desulfurization treatment was subjected to flash separation to remove the normally gaseous components including hydrogen sulfide.

The normally liquid components thus desulfurized were passed at a liquid hourly space velocity of 4 and at a pressure of approximately 300 p.s.i.g. over Attapulugus "clay treating" clay. The effluent after cooling to approximately 100° F. and pressure adjusted to substantially atmospheric pressure was distilled by careful fractionation into fractions including benzene, toluene and xylene. Of these purified aromatics, the distribution was 70.5% benzene, 22.6% toluene and the remainder xylene and C₉+ aromatics, and constituted approximately 95.5% of the aromatics originally present in the charge. Upon analysis, the benzene showed less than 5 parts per million of sulfur as thiophene, a freezing point of 5.51° C. and a bromine index of 2.9.

While it is possible to effect the desulfurization without removal of the arsenic, it is impractical in that the hydrodesulfurization catalyst life is shortened to an impractical level. Thus the arsenic removal step is necessary for practical and economical reasons.

A further illustration of the multi-stage process is given in the following example:

EXAMPLE III

A light oil charge having the following composition—

C ₆ , C ₇ , C ₈ and C ₉ benzenes	92.1 vol. percent.
Hydrocarbon impurities	6.8 vol. percent.
Thiophenes	1.1 vol. percent.
Arsenic	150-200 parts per billion.
Bromine index	10,800.

was processed adiabatically over chromia-alumina catalyst (20% chromia, 80% alumina) at the following operating conditions:

Bed inlet temperature-----° F--	800
Bed outlet temperature-----° F--	1200-1250
Space velocity-----	0.5
Pressure-----p.s.i.g.--	30
Hydrogen to oil ratio-----	1

There was recovered as liquid 93.8 vol. percent, and as aromatics-free gas 5.7 wt. percent. Coke on the catalyst was 2.0% by weight of the light oil charge. These figures include the 2% (wt. of charge) added hydrogen. The liquid product itself contained C_6+ aromatics of 99.3 vol. percent and approximately 0.7 vol. percent hydrocarbon impurities and analyzed 15 parts per billion arsenic and 250 parts per million of thiophene.

The liquid product was passed over sulfided cobalt-molybdenum on alumina catalyst at 6 LHSV, 100 p.s.i.g., 800° F. and 5 to 1 hydrogen to oil ratio effecting removal of metals including arsenic. The effluent was then passed directly into contact with a platinum on alumina catalyst comprising 0.5% platinum and 99.5% alumina at the same conditions employed during contact with the cobalt-molybdena catalyst, with the exception that a lower space rate of approximately 3 LHSV was employed.

The product from this treatment after being freed of gaseous material was clay-treated with a heat-activated bentonite clay at 400 p.s.i.g., 360° F. and at 4 LHSV. The liquid product analyzed 99.95% by volume of aromatics. Hydrocarbon impurities amounted to less than 0.05 vol. percent. The thiophene content was about 0.3 part per million and arsenic was nil. Upon distillation there was recovered 67.4 vol. percent benzene, 24.8 vol. percent toluene, 6.8 vol. percent xylenes and 1% C_9+ aromatics. The benzene fraction had a freezing point of 5.52° C., thiophene content of 0.4 part per million and a bromine index of 0.7 and an ASTM acid wash color of 0.

EXAMPLE IV

A charge oil consisting of 90% by weight of the light oil described in Example II and 10% by weight of technical grade naphthalene (74° C. melting point and 0.25% by weight sulfur by ASTM lamp analysis) is processed under substantially the same conditions as set forth in Example II.

After the clay treatment, distillative separation of the naphthalene fraction shows a recovery of better than 95% by weight of the original naphthalene in the charge. The recovered naphthalene has a melting point above 79.5° C., comparable with a melting point of 80.22° C. for highest purity naphthalene, and by lamp analysis shows less than 0.005% sulfur.

As above indicated, effective recovery of aromatics from coke oven light oil can be obtained by a one-stage operation, provided that the process conditions hereinabove set out for such operation are carefully maintained; to wit, reactor outlet temperature in the range of 1150-1170° F. and pressures above 400 p.s.i.g., with the total gas to oil mol ratio in the range of 3.1 to 6.3. Enough fresh hydrogen is present in the recycle gas such that a hydrogen partial pressure of at least $\frac{1}{2}$ the total pressure is maintained and up to a maximum limited by economics and within the upper molar limit of 6.3. To provide the required residence time of at least 60 seconds, the liquid hourly space rate will not exceed about 1.4 volumes of oil per volume of catalyst and may be as low as 0.1. A preferred catalyst for use in the process is that prepared by impregnation with chromia (providing 5 to 40% Cr_2O_3 by weight of the finished (volatiles-free) catalyst) of a high area stabilized alumina base which has a surface area of at least 120 m.²/g. and contains 0.5 to 3.0% bentonite as stabilizer. After impregnation the catalyst is adjusted by heat or steam treated to an area of about 50-60 m.²/g.

The temperature of the charge oil introduced to the reaction should be at least 1050° F. and for practical considerations preferably can be at about the temperature of the reaction zone at the inlet region, e.g., about 1100-1110° F. The temperature in the reaction zone must be within the range of 1110-1170° F. and for best results a major portion of the reaction should take place at a temperature within the range of 1150-1170° F.

The added gas, compatible with the reaction, may consist entirely of hydrogen or may comprise, in addition to the required amount of hydrogen, normally gaseous hydrocarbons and/or gases inert to reaction at the reaction conditions, such as nitrogen. Generally, the usual operation entails the separation and partial purification of the gaseous portion of the effluent product, such purified gas contains a large portion of free hydrogen and is recycled to the process as at least a major portion of the added gas. In the preferred form of operation the compatible gas is added in an amount in the range of 3.5 to 4.5 mols to each mol of the coke oven light oil charge.

Likewise, in the preferred form of operation the space rate is in the range of 0.35 to 0.5 volume of liquid per volume of catalyst or contact mass per hour; and the preferred pressure is in the range of 500 to 800 pounds per square inch gauge.

Operation within the narrower preferred ranges is particularly beneficial in securing the highest degree of purification and the best yields of purified products. Further, it will be noted that in the lower pressure operation illustrated in Examples I to IV, short on-stream periods are employed in the initial treatment in reactors A, B and C, in the order of up to about 10 minutes with cyclic regeneration of the catalyst to remove coke deposit. By operation at the higher pressures employed in the one-stage process, long on-stream periods of weeks or more are possible without involving regeneration of the catalyst.

By the one-stage operation four major goals are accomplished; first is the removal of thiophenes which can be reduced from five-figure parts per million to an order of about 0.1 to 1.0 part per million. Since thiophene constitutes one of the most objectionable ingredients in coke oven light oils, economic reasons demand thorough but cheap removal for a high order of purity in the recovered product. Other sulfur compounds in the secondary light oil are hydrogenated to H_2S more readily than is the thiophene. These other products are so completely hydrogenated that only traces if any of these materials are to be found in the product. Secondly, with respect to the paraffinic, olefinic and naphthenic content of the light oils there is accomplished cracking, hydrocracking and dehydrocyclization into readily separable materials or useful products. The nature of the chromia-alumina catalyst is such that these reactions take place with such efficient selectivity that even several percent of such impurities are effectively converted so that less than 0.1% remains in the benzene fraction recovered from this treatment. The bromine index (indicative of the presence of unsaturates) is reduced sharply and such residual traces of unsaturates as may still exist are readily removed by simple clay treatment. The third beneficial aspect lies in the conditions of operation which are such that it is possible to hydrocrack substituted aromatics to benzene, thus increasing the yield of a highly desirable product in these light oils. For instance, the process may treat a light oil containing about 60% by volume of benzene while the product may contain in the order of 80% of benzene based on the charge. The C_8 and C_9 aromatics are virtually removed and toluene is significantly reduced. The fourth advantage is in the removal of arsenic, which may be present in the charge in quantities of up to approximately 100 to 200 p.p.b. (parts per billion), to a product level in the order of <1 p.p.b. A subsequent clay treatment not only removes the traces of unsaturates as described above but removes any last measurable traces of arsenic as well.

Referring now to FIG. 2, which is a diagrammatic representation of a typical embodiment of a flow pattern in accordance with the single stage concept of this invention, there is shown line 111 for the introduction of a suitable coke oven light oil which, with the required amount of hydrogen-containing gas introduced through line 112, passes through line 113 into vaporizer 114. In vaporizer 114, operated generally at a temperature in the range of about 250° F. to 600° F., depending on the pressure which is usually between 450 and 800 p.s.i.g., separation of the desired portion of the charge is effected by vaporization thereof, while any higher boiling and/or tarry materials are not evaporated and may be removed from vessel 114 through line 115. The vaporous material passes from vaporizer 114 through line 116 after any further desired adjustment of pressure, by means not shown, to heater 117 in which the temperature of the charge is raised to about 1110° F. and the heated charge is introduced through line 118 into reactor 119.

Total effluent from reactor 119 passes through line 120 and temperature reducing means indicated at 121 into the flash and stripping vessel 122 wherein all components boiling below benzene are removed through line 123. The material in line 123 may be further separated by any suitable means, not shown, into a stream predominating in hydrogen which is introduced into the H₂S scrubber 124 while the other portion comprising hydrocarbons and other normally gaseous materials is vented for any desired purpose through line 125. The gas stream, purified in the H₂S scrubber 124 and comprising the recycle hydrogen is passed through line 126 for admixture with any fresh hydrogen, as may be required or desired, introduced through line 127. The hydrogen-containing gas thereafter with suitable pressure adjustment is passed through line 112 for admixture with fresh coke oven light oil charge.

The effluent from the flash and stripper vessel 122 comprising the benzene and higher boiling products is passed through clay treater 129 for the removal of any olefinic residue, and from thence through line 130 into distillation zone 131 from which the substantially pure benzene is removed through line 132 for recovery as required. Higher boiling materials are removed from the distillation through line 133 for any further separation, treatment or the like as may be desired or required. In one embodiment these higher boiling materials may be recycled in all or in part for conversion to benzene.

In addition to the usual heating and cooling means, pumps, valves, storage tanks and the like, which are not shown, there is indicated at dotted lines 135 and 134 means for the introduction to reactor 119 of air or other regenerating medium and for the removal of products of such possible regeneration step.

A minimum temperature of 1110° F. is necessary to convert paraffinic components to other compounds of either useful or readily separable nature. At temperatures below about 1110° F. the aromatic product may contain more than about 0.1% of saturates, such as dimethyl pentane boiling in the same range as benzene and thus difficult to separate without resorting to ultrafractionation. The presence of such extraneous materials adversely affects the freezing point, i.e., purity representation, of the benzene. At outlet temperatures above 1170° F. excessive coke formation represents undesirable product loss. While temperatures as high as 1250° F. may be employed with some beneficial results with respect to the removal and/or conversion of saturates there is an increasing loss of desired products to coke and gas, and an undesirable decrease in the amount of residual thiophene removed from the product. Thus while a high degree of purification of the aromatics is obtained by operation in the temperature range of 1110° to about 1150° F., the best results are obtained when a substantial portion of the operation is effected at temperatures within the range of about 1150° to no higher than 1170° F.

With respect to the pressure limitations, while all other conditions may be in the optimum range, pressures below about 400 p.s.i.g. produce increasingly significant quantities of coke with progressive decrease of operating pressure. With respect to the upper limit, i.e., 1000 p.s.i.g., use of higher pressures is a problem because of the equilibrium considerations of the several reactions involved, particularly with respect to the relatively large concentration of aromatics in the charge, which lead to the presence of non-aromatic saturates in the product. These saturates become significant and objectionable in quantity as the pressure increases above 1000 p.s.i.g. Thus, it is possible to operate within the general pressure limits of 400-1000 p.s.i.g. to obtain a relatively high order of purity in the product; however, the extreme high purity with minimum loss of desired aromatic products to undesired by-products is obtained at its best when the pressure is preferably maintained within the range of about 500 to about 800 p.s.i.g.

The optimum production of desired product with limited loss to undesired by-products in accordance with this invention depends in large measure likewise, on very close control of the gas to oil ratio. It has been found that product purity is a direct function of contact time. Too long residence time of the charge due to a too low gas to oil ratio results in excess coke formation; also, too high a gas to oil ratio decreases the residence time to a degree that desired product purity is not obtained. As in the operation where reduced pressure has been shown to give increased coke, likewise, it has been found that gas to oil ratios below approximately 3.5 finds the conversion of product to coke increasing as the gas ratios decrease. Further, at gas to oil ratios below about 3.1 the benefits of low coke operation are no longer of practical magnitude and are to be avoided.

With respect to the catalyst requirements in the successful operation of this purification of coke oven light oils it has been found that the process is in considerable measure so highly effective because of the peculiar and particular nature of the chromia on alumina catalyst. The particular catalyst meets and effects the several requirements in the processing with a high degree of selectivity and stability. These requirements include the necessity of substantially improved ability of cracking of the non-aromatic unsaturates and/or unsaturated side chains which may be present on an aromatic nucleus at the high temperature level above indicated without making coke in excess. Likewise, relatively high temperature level requirements hold for the selective conversion of thiophene to readily removable forms to an acceptably high order of completion. The conventional chromia on alumina catalyst is too active at the required temperature conditions to meet these requirements and the employment of such conventional catalysts results in excessive coking of the benzene and in substantial loss of desired product to undesired coke and by-products other than coke. A particularly favorable catalyst type is that described in copending application of E. B. Cornelius et al., Serial No. 660,224, filed May 20, 1957, now U.S. Patent No. 2,956,030, granted October 11, 1960. The catalysts are characterized as made by impregnating with chromia a high area porous gamma alumina with surface area in the range of at least 120 square meters per gram containing stabilizing agent comprising at least 0.5 up to about 3% swelling bentonite and preferably containing an alkali metal content measured as the oxide in the range of 0.15% to 0.5% by weight of the catalyst so as to provide 5 to 40% chromia, as Cr₂O₃, by weight of the finished catalyst. Subsequent calcination of the impregnated product reduces surface area to below 100 m.²/g. This particular catalyst is characterized in having a high degree of stability at the high operation temperatures here described against sintering and/or conversion of the active gamma alumina support to the inactive alpha form. Likewise, the presence of the

alkali metal and the stabilizing amounts of swelling bentonite have been found to moderate the activity of this catalyst to a practical low and effective degree whereby the operating conditions employed in conjunction with the catalyst give the product with the unusual and specially high purity at least an order of magnitude better than has been previously obtainable except at conditions resulting in the substantial loss of desired products. This process results in remarkably little loss and may even show some gain in desired products in comparison to the useable aromatics in the starting material.

Another suitable catalyst form is that prepared from beta alumina trihydrate treated to an alumina with a surface area of 100 m.²/g. or higher as up to 200 m.²/g. Such alumina is composited with 5-40% Cr₂O₃, preferably 15-25% such as 20% Cr₂O₃, and thereafter suitably heat treated to a surface area of no less than 50 m.²/g. As in the case of the catalyst previously described the alumina may have incorporated therein, prior to such compositing with the chromia, suitable amounts of stabilizing agent such as swelling bentonite in an amount in the range of 0.5 to 3.5% by weight and/or an alkali metal content measured as the oxide in the range of 0.15 to 0.5% by weight.

One form of the chrome-alumina catalyst of desired selectivity and low coking characteristics required for practice of the one-step refining method is prepared by the methods described in the patent application identified above.

These catalysts can be distinguished over the usual chrome-alumina catalysts heretofore extensively employed in dehydrogenation and in hydroforming operations by the following characteristics. The presence of the added bentonite, the greater resistance of the catalyst to sintering at elevated temperatures, plus a physical manifestation evident in X-ray analysis that strong $\alpha(\text{Cr}, \text{Al})_2\text{O}_3$ lines are absent in the X-ray spectra after such catalyst has been subjected to heat treatment of 1600° F. for 2-6 hours in an atmosphere of 20% steam-80% air are useful features in characterizing a useful catalyst.

The success of the one-stage process depends chiefly upon operating within the narrow temperature range described at which substantially complete conversion of thiophenes is achieved, and the provision of ample reaction time in the reactor to effect the desired conversion without excessive degradation of desired liquid products. The reaction time is related to the "nominal residence time" of the hydrocarbon charge based on an empty reactor, which in turn is a function of throughput rate, temperature and pressure, which can be formulated—

$$\theta = 3600 \cdot \frac{MW \cdot P}{L \cdot \rho \cdot (1 + G) \cdot T \cdot R}$$

in which θ is the reaction time in seconds, MW is the average molecular weight of the liquid oil charge, P is the total absolute pressure, L is the liquid hourly space velocity of the oil charge, ρ is the density of the liquid oil charge, G is the gas to oil mol ratio, T is the absolute temperature and R is the gas constant. For example when c.g.s. units are employed, R is 82.07 cc. atmospheres per gram mol per degree Kelvin.

Since the reaction is somewhat exothermic, the highest temperatures will prevail at the products outlet end of the reactor bed. To maintain the required outlet temperature in the described range of 1150-1170° F., under the prescribed operating conditions the feed should be heated to about 1050° F. or preferably to about 1100-1110° F. The average bed temperature will then lie within about 10° of the outlet temperature. With the temperature thus fixed in a rather narrow range, it will be seen that the required residence time can be obtained by controlling the pressure and space rate with reference to the gas/oil mol ratio. With the pressure limited in the

range of 400 to 1000 p.s.i.g. and the gas/oil mol ratio fixed between the limits of 3.1 to 6.3, the space rates will vary from about 0.1 to about 1.4. In general, space rates below about 0.3 are not advocated because of the low throughput rates, so that in order to obtain the required residence time it is preferred to increase the space rate above 0.3 and compensate by increasing the pressure in required amount within the described range.

Within the prescribed limits of operating conditions, the nominal residence time will lie in the range of at least 60 to approximately 180 seconds. The required minimum hydrogen partial pressure, which assures low coking operation is readily maintained by adding fresh hydrogen to the recycled gas in the amount to provide a quantity of free hydrogen initially equal to at least fifty percent of the total reactor pressure.

As previously noted thiophene is particularly refractory and is also separable from benzene only with extreme difficulty by physical means; therefore, the selective removal of thiophene as herein obtained, with no substantial destruction of useful aromatics, to such a successfully high level is a surprising and useful discovery. With respect to the conversion of such thiophene at temperatures below about 1110° F. the hydrogenation rate with this catalyst is so low that equilibrium is not reached at the desired conditions of space rate and pressure. As the temperature decreases, naturally, the approach to equilibrium is even less. However, at and above about 1140° F. the equilibrium at 400-1000 p.s.i.g. has been found to be in the desirable range and the thiophene in the product is in the acceptable range of 0.11 p.p.m. (parts per million) or less at a reaction rate sufficiently rapid that equilibrium is closely approached if not completely reached. By the same considerations, at temperatures above about 1170° F. the equilibrium value may be no less than 1 p.p.m. and will increase with increasing temperature; therefore, while the reaction rate is more rapid at the high temperatures, even reaching the equilibrium value is without merit in that these equilibrium values are not sufficiently and attractively low.

The pressure of 800 p.s.i.g. is mentioned above as the preferred upper limit and it is known that the equilibrium thiophene content can be reduced by pressure increase above the 800 p.s.i.g. level; however, the increase in efficiency of hydrogenation of thiophene must be balanced by the avoidance of the hydrogenation of benzene which tends to increase as the pressure is increased. This balance is better obtained when the pressure is held at or below about 800 pounds per square inch. Another factor in connection with the selective hydrogenation of thiophenes concerns the gas to oil mol ratio. While at higher gas to oil ratios the equilibrium value decreases, the increase in the amount of gas decreases the residence time which would require compensation to meet the minimum requirement of 60 seconds. Therefore, the upper limit of the gas to oil ratio is held to no greater than 6.3 mol ratio to prevent impractical reactor sizes and uneconomical gas volumes.

An outstanding improvement in the present operation is that with the present operation with many charge stock secondary light oils there is no particular need of the pretreatment of the charge. Since the charge itself may require no special pretreatment, the introduction of charge to the catalyst at the specified operating conditions requires simply pre-heating and admixing with the required amount of diluent gas. It is to be understood, however, that pretreatment of the charge is within the purview of this invention if such practice appears desirable to effect a measure of control of one or more possible contaminants.

While the space velocity is somewhat lower than heretofore considered normal, this limit is hardly a penalty in that the slightly longer contact time required and the resultant moderate increase in the reaction zone size is more than off-set by the substantial improvement in the

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recovered product. No pre-polymerization step normally is necessary and the coke oven light oil can be vaporized at the operating pressure in the presence of the added gas and charged directly to the catalyst. In the pre-heat operation which is non-catalytic no substantial loss of charge results and such materials as may be converted in the pre-heating step may be easily separated and removed either from the charge, if desired, or from the pre-heat zone, if required.

A fuller understanding of the operation of this invention will be readily ascertained from the following examples which are indicative of the beneficial nature of the invention without being presented as definitely limiting either the scope of the operation or the nature and extent of the operation.

EXAMPLE V

A typical coke oven light oil charge identified below was pre-heated at temperature of 375° F. in the presence of a total reactor inlet gas, comprising 0.7 mol fresh H₂ per mol of charge and the remainder recycle gas, in the ratio of approximately 5.55 mols per mol of charge was passed over the special chromia on alumina catalyst prepared as described below:

The catalyst was prepared by thorough admixing for 30 minutes the following designated materials in the proportions set forth.

Parts by weight	
Alumina trihydrate (0.35% Na ₂ O)-----	198.7
Volclay (sodium bentonite)-----	1.3
Nitric acid (20° Bé.)-----	29.0
Water -----	8.0

The mix was permitted to age for 44 hours and extruded under pressure through a die plate having 4 mm. perforations, the strands being cut to approximately 4 mm. lengths. The obtained pellets were rapidly dried in air at 270° F. and then heat-treated in dry air for 1 hour at 800° F. The pellets, after this treatment, had a bulk density of 0.80 kg./liter, a surface area of 188 square meters per gram, and a crushing strength above 31 pounds.

A solution of CrO₃ of 1.469 specific gravity (at 20° C.) containing 698 grams CrO₃ per liter, was cooled to below 5° C. and admitted into a receiver containing the above pellets (188 m²/g.) which had also been separately cooled to about the same temperature. The liquid was permitted to remain in contact with the pellets for one hour while keeping the system cool, then the pellets were drained and dried at 250° C. for 2 hours. The pellets contained approximately 20% Cr₂O₃ and about 0.45% NO₂O on an ignited alumina basis. The dried catalyst was heat-treated first in an atmosphere of dry air at 1200° F. and then at 1600° F. for 2 hours in an atmosphere of 80% air and 20% steam. The surface area of the heat-treated catalyst was approximately 55 square meters/gram.

The coke oven light oil was identified by the following properties.

Boiling range, ° C-----	About 60 to about 150
Sulfur, wt. percent (including thio.S) -----	0.55
Composition, vol. percent:	
Benzene -----	60.3
Toluene -----	22.6
C ₈ aromatics-----	7.9
C ₉ aromatics-----	1.3
Indene -----	0.4
Indane -----	0.8
Paraffins -----	1.5
Olefins+naphthenes+thio-phenes -----	5.2

The operating conditions included pressure of 500 pounds per square inch, an average bed temperature of about 1150° F., a liquid hourly space velocity (LHSV) of 0.52, and the above mentioned gas to oil ratios. The

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overall balance of this type of operation indicated that the charge comprised approximately 98.3 wt. percent of light oil and about 1.7 wt. percent charge gas, and the recovered product comprised 90% liquid, 5.8% high pressure flash gas, 2.2% atmospheric flash gas, minor amounts of carbonaceous deposits and small amounts of unaccounted for materials. The liquid analysis showed the presence of approximately 72% benzene, 22% toluene, approximately 5% C₈+benzenes, trace amounts of unsaturates, less than ½% of non-aromatic saturates and the balance mainly aromatic nucleous materials. Fractionation for the separation of benzene from non-benzene portions of the liquid product gave a benzene having the following analysis.

15 Thiophene, p.p.m-----	0.89
Bromine index-----	62.9
Chromatograph (mol percent):	
Dimethyl pentane-----	0.05
Dimethyl cyclopentane-----	0.02
20 Benzene -----	99.90
Unident.C ₆ or C ₇ -----	0.03

After simple clay treatment the benzene had a bromine index of less than 1.0, no measurable amounts of non-benzene components other than thiophene, and less than trace amounts of arsenic.

EXAMPLE VI

A light oil charge having the same composition as in Example V was processed over the catalyst of Example V at the following operating conditions: average outlet temperature of 1160° F., fresh hydrogen to oil mol ratio of 0.86, reactor inlet gas to oil mol ratio of 4.60 and a liquid hourly space velocity of 0.5. The effluent liquid was 89.6 wt. percent, the high pressure flash gas (saturated with aromatics) was 8.7 wt. percent, the atmospheric flash gas saturated with aromatics was 2.6 wt. percent and unaccounted material, coke and the like amounted to 1.1% by weight. The analysis of the liquid showed 80.3 vol. percent benzene, 17.2 vol. percent toluene, 2.2 vol. percent C₈ benzenes and the total vol. percent of other components was 0.3%. Upon simple distillation of the benzene from the liquid product the analysis of the benzene showed a benzene purity of 99.99+% and athiophene content of 0.2 p.p.m.

In connection with this example it is to be noted that the charge stock contained approximately 150 p.p.b. (parts per billion) of arsenic and the liquid effluent upon analysis showed less than approximately 1 p.p.b. The catalyst was apparently immune to poisoning by the arsenic removed from the charge stock and likewise was apparently unaffected to any noticeable degree by the small amounts of coke deposited thereon in that in a run of approximately 185 hours there was no noticeable diminution of the activity of the catalyst as reflected either in selectivity or in the quality of recovered products as measured by the quantity and quality of products recovered after 7 full days of operation.

It is evident from these examples that extremely high yields and readily recoverable desirable products can be obtained by operating in accordance with this invention. Inasmuch as operation within the scope of the suggested prior art, excepting that the conditions herein employed would be employed with such catalysts as the prior art had available, would lead to excessive destruction of benzene in the charge and the catalyst would accumulate excessive amounts of coke, so that even the better of such previously available operations would be at best a non-continuous type of operation, whereas the present type of operation can be continued for extended periods of many days, such as a month or more, without serious catalyst deactivation while achieving the outstanding and unusual high yield and extremely high purity of desired product. It is likewise evident that the unique results obtained through the careful match of a particular cata-

lyst type with closely controlled operating conditions in a manner heretofore neither contemplated nor utilized gives the resultant long term operative process for removing the undesirable impurities in a new and distinct manner.

Obviously, many modifications and variations of the invention hereinbefore set forth may be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The process for the purification of coke oven light oil contaminated with non-aromatic hydrocarbons and sulfur compounds, which comprises preheating such oil to a temperature of at least 1050° F., introducing said preheated oil into a reaction zone to contact with a chromia on alumina catalyst in which said alumina contains 0.5 to about 3% bentonite and said catalyst is characterized by a surface area of at least 50 square meters per gram, effecting said contact at a temperature in the range of 1110–1170° F., at a pressure in the range of 400–1000 p.s.i.g., and in the presence of added compatible gas in an amount of at least 3.1 and no greater than 6.3 molar ratio, said gas containing sufficient free hydrogen initially to give a hydrogen partial pressure of at least fifty percent of the total pressure of said reaction zone; said coke oven light oil being charged to said reaction zone at a space rate in the range of 0.1 to 1.4 volumes of oil (as liquid) per volume of catalyst per hour, the residence time for said oil in the reaction zone being at least 60 seconds and no more than 180 seconds, recovering normally liquid hydrocarbons from the effluent from said reaction zone, treating such liquid hydrocarbons to remove unsaturates, and fractionating the so-treated liquid hydrocarbons to recover a benzene product containing less than one part per million of thiophenes.
2. The process in accordance with claim 1 wherein said pressure is maintained within the range of 500–800 p.s.i.g.
3. The process in accordance with claim 1 wherein at least a major portion of said contact is effected at a temperature of at least 1150° F. but no greater than 1170° F.
4. The process for the purification of coke oven light oil with substantial conversion of alkylated benzenes to benzene and recovery of a benzene product containing less than 1 part per million thiophenes, comprising contacting such oil in preheated state with catalyst in a reaction zone at a temperature in the range of 1150–1170° F., a pressure in the range of 500 to 800 pounds per square inch gauge, in the presence of a hydrogen containing gas maintained within the limits of 3.5 to 4.5 mols of gas per mol of fresh oil and which gas as introduced includes free hydrogen in an amount to maintain a minimum hydrogen partial pressure of at least 250 pounds per square inch, utilizing space rates such that the residence time of the coke oven light oil in the reactor is no less than 60 seconds and no more than 180 seconds; said catalyst being that obtained by compositing 15–25% Cr₂O₃ on alumina, said alumina before compositing consisting of a high area alumina base having at least 120 square meters per gram surface area and containing 0.5 to about 3.0% bentonite and the obtained catalyst composite subsequently being area adjusted by heat treatment to 50–65 square meters per gram.
5. The process for the purification of coke oven light oil comprising vaporizing such oil by preheating the same in the presence of a hydrogen-containing gas to a temperature in the range of 250 to 600° F. and at a total reactor pressure in the range of 500 to 800 pounds per square inch gauge, further heating said vaporized oil charge and introducing said further heated charge to reaction at an introduction temperature in the range of 1100–1110° F. into contact with a chromia on alumina catalyst characterized in having 15–25% Cr₂O₃ impreg-

nated on high area alumina derived from beta alumina trihydrate, said alumina having a surface area of 100 to 200 square meters per gram before impregnation and said catalyst being heat treated after impregnation to adjust the surface area thereof to no less than 50 square meters per gram; maintaining the temperature of said reaction within the range of said introduction temperature and an outlet temperature in the range of 1150–1170° F. so that during a portion of said reaction the charge is subjected to at least 1150° F., said reaction being effected in the presence of hydrogen containing gas at a total gas to oil mol ratio of at least 3.1 but no greater than 6.3, said gas initially containing free hydrogen in an amount constituting at least fifty percent of said total reactor pressure, said charge being introduced at a space rate in the range of 0.35 to 0.5 volume of oil (as liquid) per volume of catalyst per hour, the residence time being within the range from 60 to 180 seconds, passing the effluent from said reaction with intervening pressure and temperature reduction to a separation zone, separating said effluent into a first fraction containing substantially all products boiling below the boiling point of benzene and a second fraction containing products boiling in the range of benzene and higher; passing said first fraction to separation and purification zones and recovering therefrom at least one gas stream comprising hydrogen; passing said second fraction to clay treatment to remove residual non-aromatic hydrocarbons and passing said clay-treated fraction to further fractional distillation and recovering therefrom at least one fraction consisting of benzene containing less than one part per million of thiophenes and having a bromine index less than one.

6. The process for the purification of coke oven light oil to obtain therefrom substantially pure aromatics comprising preheating such a light oil to a temperature of about 1110° F., passing such preheated oil at an inlet temperature of at least 1110° F. over a solid contact mass in a reaction zone at a space rate in the range of 0.1 to 1.4 volumes of oil (as liquid) per volume of contact mass per hour and under a total pressure in the range of 500–800 pounds per square inch gauge in the presence of an added compatible gas at a gas to oil mol ratio of at least 3.5 to 1.0, said gas containing sufficient free hydrogen initially to give at least fifty percent of said total pressure, said passing providing a residence time from 60 to 180 seconds; said contact mass being one prepared by impregnating porous activated alumina with surface area of 100 to 200 square meters per gram with 15–25% chromia (as Cr₂O₃) by weight of said mass, effecting said contact at a temperature above 1110° F. but no higher than 1170° F.; separating the effluent from said reaction zone into fractions including a fraction comprising benzene and higher boiling aromatics, treating said fraction to remove therefrom non-aromatic hydrocarbons, and subsequently treating said non-aromatics free fraction to separate and recover therefrom benzene having a bromine index less than one and containing less than one part per million of thiophenes.

7. The process in accordance with claim 6 wherein said contact mass is characterized in containing a stabilizing agent comprising at least 0.5 to about 3% swelling bentonite and further characterized in containing an alkali metal content, measured as the oxide in range of 0.15 to 0.5%, said percentages each by weight of said contact mass.

8. The process in accordance with claim 6 in which said contact is effected at an average bed temperature within about 10° of and no higher than the outlet temperature, said outlet temperature being in the range of 1150–1170° F.

9. The process for the selective hydrogenation of sulfur compounds including thiophene in coke oven light oils comprising contacting such a sulfur-containing light oil at reaction conditions including a temperature in the range of 1150–1170° F., a pressure in the range of 500–800 p.s.i.g., in the presence of hydrogen containing gas main-

tained within the limits of 3.5 to 4.5 mols per mol of fresh oil charge, said gas including free hydrogen in an amount maintaining a minimum hydrogen partial pressure above at least one-half of the total pressure in said reaction, utilizing a space rate in which the nominal residence time of said charge in said reactor is not less than 60 seconds nor more than 180 seconds, utilizing a contact mass comprising 15-25% chromia on an alumina containing approximately 1% bentonite, said contact mass having a surface area of approximately 50-65 meters per gram, separating hydrogen sulfide from the effluent in said reaction and recovering benzene containing less than one part per million of sulfur.

10. The method of treating coke oven light oil for recovery of purified aromatic hydrocarbons therefrom, said oil having contaminants including sulfur compounds, heavy metals and non-aromatic hydrocarbons, which method comprises subjecting such oil to contact with solid dehydrogenation catalyst under conditions effecting dehydrogenation of non-aromatics without significant saturation of the aromatic hydrocarbons, removing heavy metal contaminants by passing the effluent in vapor phase over an adsorptive porous contact mass capable of retaining arsenic compounds and thereafter desulfurizing at least the normally liquid portion of the thus demetallized effluent by contact in vapor phase over hydrogenation catalyst at 725° to 1000° F. in the presence of hydrogen; and removing from the desulfurized liquid product normally gaseous products and olefin products formed by said dehydrogenation and desulfurization.

11. The method of treating coke oven light oil for recovery of purified aromatic hydrocarbons therefrom, said oil being contaminated by sulfur compounds, arsenic and non-aromatic hydrocarbons, which method comprises subjecting such oil to contact with solid dehydrogenation catalyst under conditions effecting dehydrogenation of non-aromatics without significant saturation of the aromatic hydrocarbons, passing the effluent from said dehydrogenation contact into contact with sulfided cobalt molybdena supported on alumina catalyst at conditions of temperatures in the range of 725° to 1000° F., a liquid hourly space velocity in the range of 1 to 25, added hydrogen in the range of 2 to 10 mols/mol of oil, and at a hydrocarbon partial pressure in the range of 0.4 to 10 atmospheres, effecting by said last mentioned contact substantially complete removal of arsenic contaminants, thereafter desulfurizing at least the normally liquid portion of said arsenic-free effluent by contact in vapor phase over hydrogenation catalyst in the presence of hydrogen and at a temperature in the range of 725° to 1000° F.; further treating the effluent from said desulfurization to remove normally gaseous products and olefinic products formed by said dehydrogenation and desulfurization; and recovering normally liquid purified aromatic hydrocarbon product.

12. The process of purifying a coke oven light oil composed chiefly of aromatic hydrocarbons boiling substantially in the range of benzene through xylene, which

process comprises the steps of: catalytically dehydrogenating non-aromatic contaminants in the oil without significant saturation of the aromatics, said dehydrogenation being effected over chromium oxide-alumina catalyst in the presence of hydrogen added in the range of up to 4 mols per mol of said oil charge, at an inlet temperature in the range of 700° to 1100° F., with a liquid hourly space velocity in the range of 0.2 to 2.0, and at a pressure in the range of 0.4 to about 40 atmospheres; contacting at least the normally liquid portion of the effluent from dehydrogenation at a temperature in the range of 300° to 375° F., at a liquid hourly space velocity in the range of 1 to 6 and at a pressure in the range of 10 to 50 atmospheres with an adsorptive contact mass, said contacting selectively removing residual dehydrogenated products of said dehydrogenating treatment; and recovering purified aromatic hydrocarbons from said contacting.

13. In a process for the purification of coke oven light oil contaminated with significant amounts of non-aromatic hydrocarbons and sulfur compounds, in which process the coke oven light oil is vaporized and the light oil vapors admixed with a hydrogen-containing carrier gas so that the mixture contains significantly more hydrogen by volume than light oil vapor and the mixture is converted over a chromia-on-alumina catalyst at elevated pressure and temperature to produce an effluent from which a liquid product is recovered, and the liquid product is separated to recover a benzene fraction having a smaller content of non-aromatic hydrocarbons and smaller content of sulfur compounds than the coke oven light oil, the improvement which includes the combination of: preheating the mixture of hydrogen-containing gas and vapors of light oil to a temperature more than 1050° F. but less than 1110° F.; maintaining a fixed bed of chromia-alumina granules containing more than 15% but less than 25% Cr₂O₃ at an average bed temperature of at least 1110° F. but less than 1170° F., whereby the effluent from the fixed bed of catalyst has a temperature within the range from 1110 to 1170° F.; said catalyst being the product obtained by chrome impregnation of a high area alumina base of 100-200 m.²/g. surface area derived from beta alumina trihydrate; regulating the residence time of the mixture of hydrogen-containing gas and light oil vapors within the range from 60 to 180 seconds; withdrawing a benzene product containing less than one part per million of thiophenes by reason of such control of the temperature, residence time, and chromia concentration of the catalyst granules; and continuing such purification of light oil for a prolonged period before regeneration of the catalyst by reason of the formation of small amounts of carbonaceous deposit in the catalyst bed.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,081,259

March 12, 1963

Joseph J. Donovan et al.

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

Column 2, line 20, for "referred" read -- preferred --;
column 4, line 63, for "is" read -- in --; column 7, line 75,
for "50-60" read -- 50-65 --.

Signed and sealed this 12th day of November 1963.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

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Acting Commissioner of Patents