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PRODUCTION OF ISOPARAFFINS

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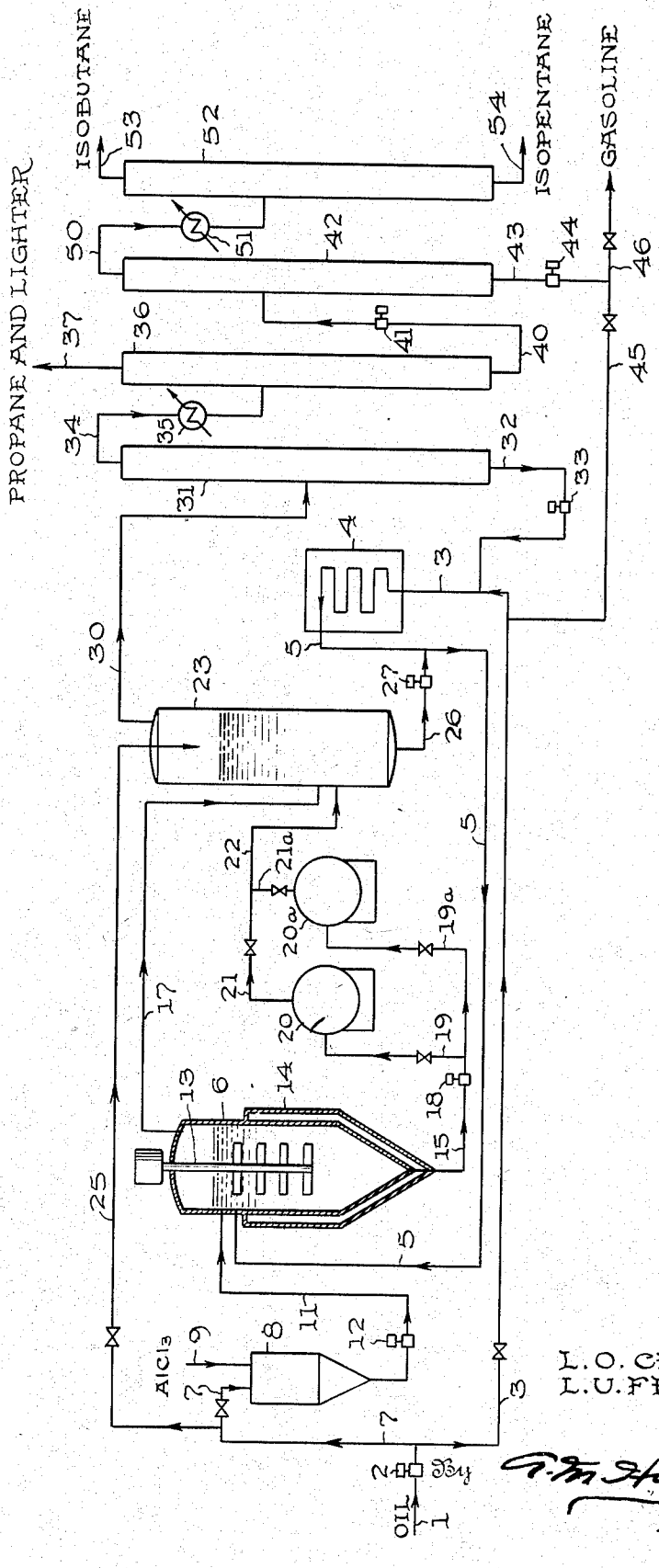

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PRODUCTION OF ISOPARAFFINS

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5 Claims. (Cl. 260—683.5)

This invention relates to the production of isoparaffins; and it comprises a process wherein a petroleum oil is heated in a conversion zone with about 10 to 20 per cent by weight, on the petroleum oil momentarily in the conversion zone, of aluminum chloride at about 450° to 750° F., scrubbing the vapors of conversion products with at least a portion of the charge oil and condensing aluminum chloride contained therein and returning it to the conversion zone, and condensing and returning to the conversion zone at least a portion of the higher boiling conversion products; all as more fully hereinafter described and as claimed.

Isobutane and isopentane are useful in the production of high octane gasoline. Thus either of these lower isoparaffins, upon alkylation or condensation with a lower olefin, yields a mixture of branched chain paraffins much of which boils in the gasoline boiling point range and has a high octane number. The demand, however, for these lower isoparaffins exceeds the supply.

Economical methods of producing isobutane and isopentane are much sought after. One method of producing them comprises distilling a petroleum oil in the presence of aluminum chloride. The distillate comprises some isobutane and isopentane, but also much gasoline and kerosene or higher boiling material. The production of isobutane and isopentane, particularly the former, can be increased somewhat by effecting the distillation at a higher temperature. However, difficulties result from this expedient. For one thing, considerable vaporization of the aluminum chloride occurs. As a result, catalyst is lost from the reaction zone and the rate of conversion drops. Also, the aluminum chloride vapor recondenses in cooler portions of the apparatus, causing stoppage of lines, valves and the like. The aluminum chloride vapor is also corrosive toward refinery equipment.

The production of isobutane and isopentane by distilling petroleum oils in the presence of aluminum chloride, because of low yields and other difficulties heretofore met with, has not been economical.

It is an object achieved by the present invention to produce isobutane and isopentane economically from petroleum oils.

We have achieved this object by heating a petroleum oil, advantageously a paraffinic petroleum oil, with about 10 to 20 per cent by weight, on the petroleum oil momentarily in the conversion zone, of aluminum chloride at about 450° to 750° F., scrubbing the vapors of conversion products with fresh charge oil and condensing aluminum chloride vapor contained therein and returning the condensed aluminum chloride to the conversion zone, and condensing and returning to the conversion zone at least a portion of the higher boiling conversion products.

The method of our invention will be better understood by reference to the accompanying more or less diagrammatic drawing, which represents an advantageous embodiment of the invention.

Referring to the drawing, a charge oil, advantageously a paraffinic petroleum oil, is pumped into the system through a line 1 by a pump 2. Part of this stream of oil is passed through a valved line 3 to a heater 4 (which may be a furnace, a heat exchanger, or any other suitable heating means). In heater 4, the oil is preheated to about 500° to 800° F. and the preheated oil is passed through a line 5 into the top portion of a primary reaction vessel or still 6. Another portion of the charge oil entering through line 1 is passed through a valved line 7 into a mixing vessel 8. Anhydrous aluminum chloride is introduced into vessel 8 through a line 9. In vessel 8 the aluminum chloride and oil are vigorously mixed by suitable means (not shown) to produce a slurry of aluminum chloride in oil and this slurry is pumped through a line 11 by a pump 12 into reaction vessel 6.

Reaction vessel 6 is provided with a stirrer 13 and a heating jacket 14. The mixture of aluminum chloride slurry and preheated oil are vigorously intermixed therein by stirrer 13 and are maintained at about 450° to 750° F., advantageously 550° to 650° F., by means of heating jacket 14. Liquid mixture is withdrawn from the bottom of vessel 6 through a line 15, conversion products are distilled and removed from vessel 6 through a line 17 and charge oil and aluminum chloride are added, as described, at such rates as to maintain a steady, rapid production of isobutane and isopentane and to maintain about 10 to 20 per cent by weight, on the oil in vessel 6, of aluminum chloride, and so as to prevent coking in vessel 6. The withdrawn oil containing aluminum chloride is pumped by pump 18 alternately through a valved line 19 to a coking still 20 and through a valved line 19a to a coking still 20a. These chambers 20 and 20a are sometimes known as the coking zone. While the mixture is being pumped to one or the other of the coking stills 20 or 20a and is heated therein to coking, the other coking still is decoked. Conversion products are removed from coking still

20 or 20a through a valved line 21 or 21a, respectively, and introduced through a line 22 into the bottom portion of an absorption vessel 23. This vessel 23 is sometimes known as the activating zone. Conversion products from vessel 6 are also introduced, through line 17, into the bottom portion of absorption vessel 23.

A portion of the charge oil pumped through lines 1 and 7 is diverted through a valved line 25 and introduced into the top portion of absorption vessel 23. In this vessel, a relatively low temperature, advantageously about 200° to 350° F., is maintained by means of the cool charge oil or by other cooling means, or both, whereby substantially all of the aluminum chloride vapor contained in the conversion products condenses and dissolves in or forms a slurry with the charge oil. In addition to condensing aluminum chloride, vessel 23 may be so operated that any desired portion of the conversion products is also condensed therein. Thus everything boiling higher than isopentane, or everything boiling higher than gasoline or kerosene may be condensed in vessel 23 and only the lower boiling products allowed to go forward. Advantageously, substantially all of the gasoline is allowed to go forward and is recovered as subsequently described. The resulting mixture of charge oil and aluminum chloride, or of charge oil, aluminum chloride, and certain of the conversion products, is pumped from the bottom of vessel 23 through a line 26 by a pump 27 into line 5 and thus back into reaction vessel 6.

The benefits obtained by the procedure as thus far described are principally these: Because of the optimum temperatures and aluminum chloride concentrations used in the low temperature, non-coking conversion zone (reaction vessel 6), the optimum combination of high yield of isobutane and isopentane with low vaporization of aluminum chloride is obtained therein. Higher concentrations of aluminum chloride and higher temperatures would produce more isobutane and isopentane, but coking would result in the main still (thus causing shutdowns at frequent intervals) and the loss of aluminum chloride therefrom by vaporization would be higher than justified by the increased yield of isobutane and isopentane. On the other hand, lower temperatures and lower concentrations of aluminum chloride in the main still would result in less vaporization of aluminum chloride, but this result would not justify the reduced yield of isobutane and isopentane. Moreover, the means described to recover the aluminum chloride is the most economical and advantageous and it results in activation of the charge oil, perhaps by organic halides or other halides contained in the conversion products and absorbed therefrom by the charge oil.

Furthermore, a fargoing ultimate recovery of aluminum chloride, and a simultaneous production of HCl or organic chlorides or both, are effected in a continuous manner, not affecting the course of reaction in the main low temperature still, by the separate coking stills. In any process involving treatment of oils with aluminum chloride a certain waste of aluminum chloride results, it being combined with the oil in a manner which inactivates it as a catalyst. By the process of the present invention, as illustrated above with reference to the drawing, a part, advantageously the major part. of the conversion is carried out at lower temperatures, without coking, and therefore with a catalyst of maximum activity. The used (but not completely spent) catalyst is withdrawn as a slurry and coked separately, the higher temperature involved in coking thereby in part, at least, obviating the lessened activity of the catalyst and also freeing aluminum chloride as vapor and driving it off with some HCl or organic chloride or both. The thus freed and regenerated aluminum chloride is recovered, as described, and recycled, as is also part, at least, of the HCl or organic chloride, or both.

Returning to the description of the process, absorption vessel 23 is advantageously operated so that all but the aluminum chloride vapor and the heaviest (practically unconverted) oil do not condense but go forward. To accomplish this, the stated temperature of 200° to 350° F. and a pressure of about 5 to 15 pounds per square inch gauge are advantageously maintained in vessel 23. As shown in the drawing, these uncondensed products are passed through a line 30 to a fractionating column 31. In column 31, the mixture is fractionated into an overhead of gasoline and lighter material and a bottoms of higher boiling oil. This bottoms is pumped through a line 32 by a pump 33 into line 3 and thus through heater 4 and line 5 back to conversion vessel 6. The overhead of column 31 is passed through a line 34 containing a condenser 35 to a fractionating column 36 wherein it is fractionated into an overhead of propane and lighter material and a bottoms of isobutane and heavier hydrocarbons. The propane overhead is vented from the system through a line 37 and the bottoms is pumped through a line 40 by a pump 41 into a fractionating column 42 wherein the mixture is fractionated into a C_4—C_5 overhead and a bottoms of gasoline. The gasoline bottoms is pumped through a line 43 by a pump 44. Any desired portion of this gasoline bottoms may be conducted through a valved line 45 to line 3 and thus through heater 4 and line 5, back to conversion vessel 6, but usually it is advantageous to remove the gasoline bottoms from the system through a valved line 46 as a valuable product of the process. However, if the desideratum is to produce the maximum amount of lower isoparaffins, all or the major part of the gasoline may be recycled to the conversion zone.

The overhead from column 42 is passed through a line 50 containing a condenser 51 into a fractionating column 52, wherein the mixture is fractionated into an isobutane overhead and an isopentane bottoms, which are removed from the system through lines 53 and 54, respectively. Any normal butane, normal pentane and olefins present in the isobutane overhead or the isopentane bottoms may be separated by further fractionation (not shown).

In an alternative method of recovering the products of the process, the depropanized bottoms from column 36 may be fractionated into a C_4 overhead and a debutanized bottoms, the C_4 overhead fractionated into isobutane and normal butane (of which the latter may contain some butylenes), and the debutanized bottoms may be fractionated into an isopentane overhead and a de-isopentanized bottoms (gasoline). The de-isopentanized bottoms may be removed from the system or recycled, or partly removed and partly recycled, as stated.

In conducting the process of our invention, we advantageously use a clean paraffinic charging stock, i. e., a stock that is relatively free from asphaltic, tarry, or other residual constituents, and which has been derived from a relatively saturated, non-aromatic crude petroleum oil, said

stock boiling between about 325° and 650° F. at 40 mm. absolute pressure. Typical preferred materials are Rodessa or other paraffinic solar distillates, foots oil and ketone slack wax, but other oils, e. g., naphthenic oils such as Gulf Coastal solar distillate, may be used. The best materials of all to use are high boiling petroleum products such as foots oil, sweat oil and wax discharge from the centrifugal dewaxing of cylinder stocks in naphtha and the like. Such materials are cheap, being produced in considerable quantities during the separation of wax from petroleum oils, and they contain a large proportion of high molecular weight isoparaffins. They are further characterized by boiling points above about 325° F. at 40 mm. absolute pressure. Such stocks are more readily converted and produce higher yields of isobutane and isopentane than other stocks.

As much as 50 per cent conversion or more, based on charge oil, to isobutane and isopentane may be obtained per pass by the process of our invention, and by recycling heavier products of conversion, even greater conversion to isobutane and isopentane can be obtained.

A small amount of hydrogen chloride, other hydrogen halide, or a substance capable of yielding hydrogen halide may be introduced into the conversion zone to supplement that formed in the reaction itself. The rate of conversion is increased and the catalyst life is prolonged by the presence of such promoters.

In condensing the aluminum chloride from the vapors of conversion products, it is advantageous to use a temperature of about 200° to 350° F. and a pressure of about 5 to 15 pounds per square inch gauge. Under such conditions the aluminum chloride vapors are readily condensed without condensing much of the conversion products.

The following specific example will further illustrate the practice and advantages of our invention:

A charge oil is used consisting of foots oil produced by sweating acid treated slack wax. This foots oil charge had the following inspection:

Gravity: °A. P. I.		36.6
Distillation, vacuum 40 mm. abs. pressure:		
Over point	°Fahrenheit	335
End point	do	630
10 percent at	do	435
30		467
50		489
70		523
90		581
Recovery	percent	99
Residue	do	1
Loss	do	0

To a still provided with a stirrer and heating means are continuously added a feed of the above foots oil and anhydrous aluminum chloride in proportions of 100 parts by weight of the oil and 15 parts by weight of aluminum chloride. The contents of the still are vigorously stirred and maintained at 600° F. Conversion products are passed through an absorption tower in countercurrent to a portion of the above-mentioned feed of foots oil. The temperature at the top of this tower is maintained at 300° F., thereby causing substantially complete condensation of aluminum chloride vapors and of vapors of charge oil and all conversion products boiling higher than gasoline (i. e., higher than about 375° F.). The condensation products are returned to the reaction zone together with the portion of foots oil passed through the absorption tower. Oil and aluminum chloride are withdrawn from the bottom of the still at such a rate as to maintain a concentration of aluminum chloride in the still of about 15 per cent by weight on the oil therein and to prevent coking in the still. The withdrawn oil and aluminum chloride are heated to coking in a separate still and the vapors from this coking still are added to the vapors entering the above-mentioned absorption tower.

The product of such a process contains upwards of 50 per cent by weight, on the charge oil, of isobutane and isopentane and upwards of 30 per cent by weight on the charge oil of gasoline (C_5 and higher hydrocarbons boiling in the gasoline range).

In a representative case, a product (gasoline and lower boiling products) of the following composition was obtained:

Methane and hydrogen	
—22.62% by liquid volume on foots oil charged	
Ethane	0.89
Propane	11.40
Isobutane	31.37
n-Butane	7.56
Isopentane	22.82
n-Pentane	0.39
Gasoline distillate (C_5 and higher)	34.51

While our invention has been described with particular reference to certain embodiments and specific examples, it is not limited to such embodiments and specific examples except as defined in the appended claims.

What we claim is:

1. A method of producing lower isoparaffins, which comprises maintaining contact in an unfired conversion zone between aluminum chloride and a paraffinic petroleum oil in a ratio of about 1 to 2 parts by weight of aluminum chloride per 10 parts by weight of petroleum oil, maintaining in said conversion zone a temperature of about 550° to 650° F. and a pressure of about 25 to 150 pounds per square inch gauge, withdrawing a substantially uncoked mixture of oil and aluminum chloride and supplying it to a coking zone, passing the vapors from said conversion zone and said coking zone into a substantial pool of oil in an activating zone in contact with a fresh feed of paraffinic petroleum oil, maintaining in said activating zone a temperature of about 200° to 350° F. and a pressure of about 5 to 15 pounds per square inch gauge, condensing in said activating zone substantially all of the aluminum chloride in said vapors, condensing the conversion product vapors boiling higher than gasoline, returning the condensed aluminum chloride with a heated stream of fresh feed oil to said conversion zone, and returning to said conversion zone at least the major portion of the condensed conversion products boiling higher than gasoline.

2. A continuous method of manufacturing lower isoparaffins which comprises maintaining an unfired but externally heated primary reaction zone, an activating zone, and a coking zone; continuously introducing into the primary reaction zone a stream of heated hydrocarbon oil and a stream of hydrocarbon-aluminum-chloride catalyst, there reacting the oil and catalyst at a temperature of the order of 450° F. to 750° F. to convert some of the oil into hydrocarbons which are vaporized at the reaction temperature; removing a stream of oil containing used hydrocarbon-aluminum-chloride catalyst from the primary reaction zone to the coking zone and there vaporizing the hydrocarbons and residual aluminum

chloride; continuously introducing into the activation zone a first stream of paraffinic hydrocarbon charge oil, maintaining a substantial pool of oil in the activating zone at a temperature of the order of 200° F. to 350° F., and activating the said oil by introducing thereinto all of the vapors generated in the primary reaction zone and in the coking zone; continuously removing from the activating zone a stream of vapors and fractionating this stream to separately obtain the desired isoparaffins; continuously removing from the activating zone a stream of oil and aluminum chloride and conveying it to the primary reaction zone; and continuously heating a second stream of paraffinic hydrocarbon charge oil to a temperature of the order of 500° F. to 800° F. and utilizing that stream as the heated hydrocarbon oil which is introduced into the primary reaction zone with the hydrocarbon-aluminum-chloride catalyst and which constitutes the primary source of heat therefor.

3. A continuous method of manufacturing lower isoparaffins which comprises maintaining an unfired but externally heated primary reaction zone, an activating zone, and a coking zone; continuously introducing into the primary reaction zone a stream of heated hydrocarbon oil and a stream of hydrocarbon-aluminum-chloride catalyst, there reacting the oil and catalyst at a temperature of the order of 450° F. to 750° F. to convert some of the oil into hydrocarbons which are vaporized at the reaction temperature; removing a stream of oil containing used hydrocarbon-aluminum-chloride catalyst from the primary reaction zone to the coking zone and there vaporizing the hydrocarbons and residual aluminum chloride; continuously introducing into the activation zone a first stream of paraffinic hydrocarbon charge oil, maintaining a substantial pool of oil in this zone at a temperature slightly above the boiling point of the desired end product, and activating the said oil by introducing thereinto all of the vapors generated in the primary reaction zone and in the coking zone; continuously removing from the activating zone a stream of vapors and fractionating this stream to separately obtain the desired isoparaffins; continuously removing from the activating zone a stream of oil and aluminum chloride and conveying it to the primary reaction zone; and continuously heating a second stream of paraffinic hydrocarbon charge oil to a temperature of the order of 500° F. to 800° F. and utilizing that stream as the heated hydrocarbon oil which is introduced into the primary reaction zone with the hydrocarbon-aluminum-chloride catalyst and which constitutes the primary source of heat therefor.

4. A continuous method of manufacturing lower isoparaffins which comprises maintaining an unfired but externally heated primary reaction zone, an activating zone, and a coking zone; continuously introducing into the primary reaction zone a stream of heated hydrocarbon oil and a stream of hydrocarbon-aluminum-chloride catalyst, there reacting the oil and catalyst at a temperature of the order of 450° F. to 750° F. to convert some of the oil into hydrocarbons which are vaporized at the reaction temperature; removing a stream of oil containing used hydrocarbon-aluminum-chloride catalyst from the primary reaction zone to the coking zone and there vaporizing the hydrocarbons and residual aluminum chloride; continuously introducing into the activation zone a first stream of paraffinic hydrocarbon charge oil, maintaining a substantial pool of oil in the activating zone at a temperature of the order of 200° F. to 350° F., and activating the said oil by introducing thereinto all of the vapors generated in the primary reaction zone and in the coking zone; continuously removing from the activating zone a stream of vapors and fractionating this stream to separately obtain the desired isoparaffins and an undesired heavier fraction; continuously removing from the activating zone a stream of oil and aluminum chloride and conveying it to the primary reaction zone; and continuously heating a second stream of paraffinic hydrocarbon charge oil together with the undesired heavier fraction from the fractionation step to a temperature of the order of 500° F. to 800° F. and utilizing that stream as the heated hydrocarbon oil which is introduced into the primary reaction zone with the hydrocarbon-aluminum-chloride catalyst and which constitutes the primary source of heat therefor.

5. A continuous method of manufacturing lower isoparaffins which comprises maintaining an unfired but externally heated primary reaction zone, an activating zone, and a coking zone; continuously introducing into the primary reaction zone a stream of heated hydrocarbon oil and a stream of hydrocarbon-aluminum-chloride catalyst, there reacting the oil and catalyst at a temperature of the order of 450° F. to 750° F. to convert some of the oil into hydrocarbons which are vaporized at the reaction temperature; removing a stream of oil containing used hydrocarbon-aluminum-chloride catalyst from the primary reaction zone to the coking zone and there vaporizing the hydrocarbons and residual aluminum chloride; continuously introducing into the activation zone a first stream of paraffinic hydrocarbon charge oil, maintaining a substantial pool of oil in this zone at a temperature near the end boiling point of the desired products, and activating the said oil by introducing thereinto all of the vapors generated in the primary reaction zone and in the coking zone; continuously removing from the activating zone a stream of vapors and fractionating this stream to separately obtain the desired isoparaffins and an undesired heavier fraction; continuously removing from the activating zone a stream of oil and aluminum chloride, continuously heating a second stream of paraffinic hydrocarbon charge oil together with the undesired heavier fraction from the fractionation step to a temperature of the order of 500° F. to 800° F., combining this so heated stream with the stream of oil and aluminum chloride from the activating zone, and utilizing the combined stream as the heated hydrocarbon oil which is introduced into the primary reaction zone with the hydrocarbon-aluminum-chloride catalyst and which constitutes the primary source of heat therefor.

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