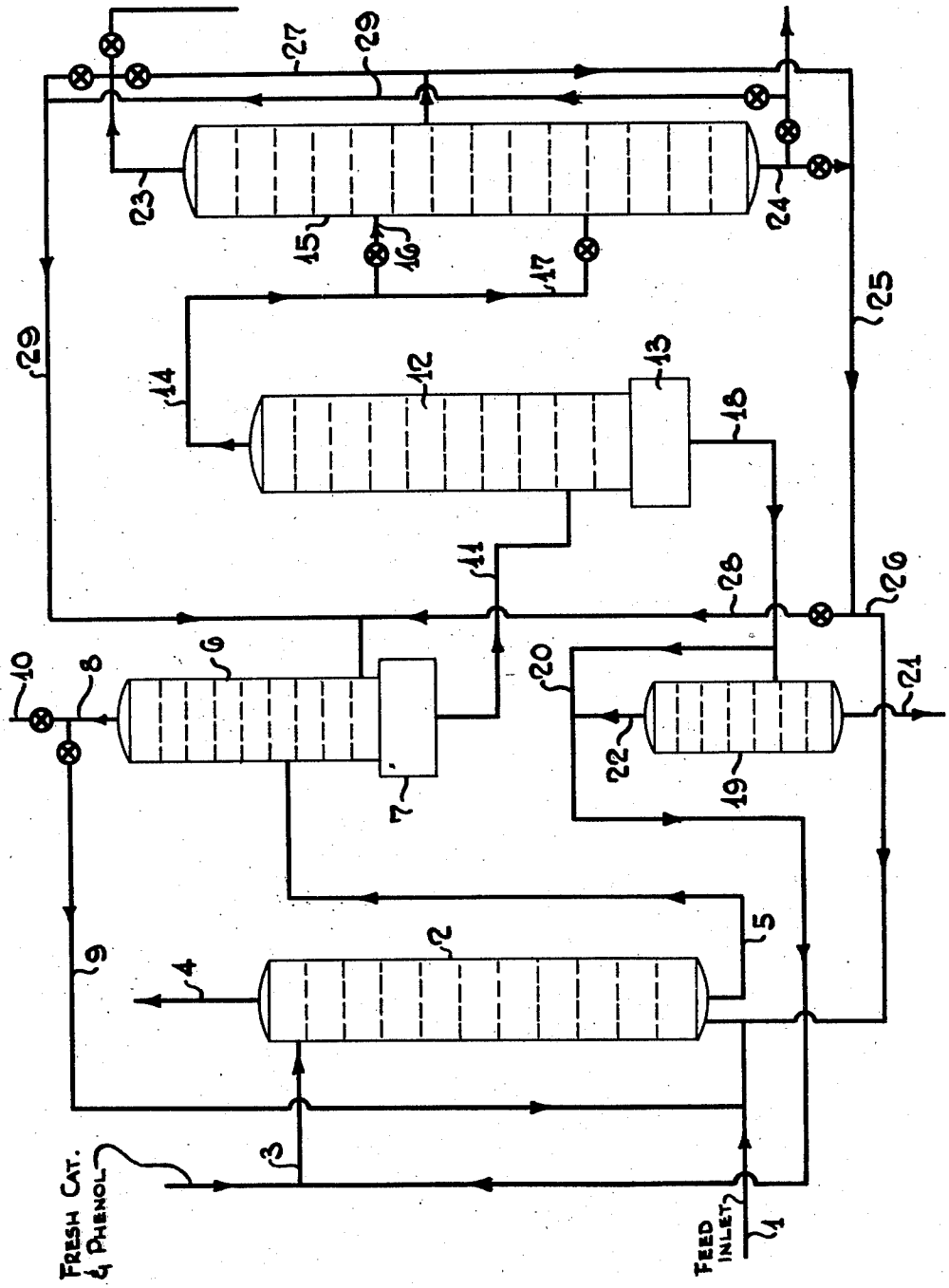
Aug. 19, 1947. L. K. BEACH 2,425,858

PROCESS FOR ISOMERIZING TERTIARY OLEFINS

Filed Sept. 27, 1944



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Patented Aug. 19, 1947 2,425,858

UNITED STATES PATENT OFFICE

2,425,858

PROCESS FOR ISOMERIZING TERTIARY OLEFINS

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Application September 27, 1944, Serial No. 555,936

10 Claims. (Cl. 260—683.2)

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This invention relates to improvements in the interconversion of isomers of tertiary olefins, and it relates particularly to the interconversion of 2-methylbutene-1 and 2-methylbutene-2.

Olefins are known to react with phenols in the presence of a catatlyst at temperatures ranging from 0° to 100° C. to form alkyl phenols and the alkyl phenols may be decomposed to phenols and olefins by the use of heat in the presence of catalysts. This method has been used for separating tertiary olefins which react more readily with the phenols, from mixtures of hydrocarbons containing both saturated and unsaturated hydrocarbons.

According to this invention it has now been found that phenols (cresols, xylenols, etc.) may be used to react with tertiary amylenes in mixtures of saturated and unsaturated hydrocarbons containing 5 carbon atoms, and that the alkylated phenols upon being decomposed by heat or reduced pressure in the presence of a catalyst to regenerate the phenol result in the formation of an equilibrium mixture of 2-methylbutene-1 and 2-methylbutene-2. It has further been found that if the undesired isomer is separated from the equilibrium mixture and alkylated with more or regenerated phenol to form more alkylated phenols, the subsequent decomposition of the alkyl phenol results in another similar equilibrium mixture of the isomers of tertiary amylenes regardless of which one was alkylated initially. This discovery allows a high yield of the desired isomer to be obtained regardless of its concentration in the feed.

Catalysts found to be more or less satisfactory for the alkylation step include all nuclear condensation catalysts, such as sulfuric acid, sulfuric esters, aromatic sulfonic acids, zinc, aluminum and tin chlorides and boron fluorides, the most satisfactory of which are benzenesulfonic acid and p-toluenesulfonic acid. For the regeneration step the same catalysts are more or less satisfactory, the most satisfactory being benzenesulfonic acid, p-toluene sulfonic acid and the alkyl esters of both.

This invention will be more readily understood on reading the following description with reference to the accompanying drawing where a mixture of saturated and unsaturated hydrocarbons of 5 carbon atoms containing tertiary amylenes is passed through pipe 1 into the bottom of alkylation tower 2 where this mixture passes in countercurrent flow at atmospheric or higher pressure to a phenol introduced into this alkylation tower 2 by means of pipe 3. The unreacted hydrocarbons are removed from the top of the tower by

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means of pipe 4 and the alkylated phenol is removed from the bottom of the tower by means of pipe 5 and passed to stripper 6. Stripper 6 also operating under pressure if desired is provided with a reboiler section 7 where steam pipes or other means of heating not shown are used to raise the temperature. From stripper 6 are removed by means of pipe 8 the hydrocarbons that have not reacted with the phenol. These hydrocarbons may be recycled by means of pipe 9 to inlet pipe 1 or may be removed from the circuit by means of pipe 10. The alkylated phenol substantially free of any unreacted hydrocarbons is then passed through pipe 11 into fractionating tower 12, operating at a pressure equal to or below those of towers 2 and 6, which is provided with a regeneration section 13 where heat is supplied by means of steam pipes or other heating means (not shown). Product tertiary olefins are distilled overhead through pipe 14 and passed into distillation column 15 by means of pipes 16 or 17. The regenerated phenol is removed from the regenerator section 13 by means of pipe 18 to flash tower 19 or bypassing the flash tower 19 through pipe 20 to phenol feed lines 3. From flash tower 19 the stream of high boiling bottoms is discarded through pipe 21 and the purified phenol passed through pipe 22 to pipe 20. From distillation column 15 an overhead product of 2-methylbutene-1 is obtained through pipe 23 and a bottoms of 2-methylbutene-2 is obtained through pipe 24. If it is desired to obtain substantially 2-methylbutene-1, the 2-methylbutene-2 obtained by means of pipe 24 may be recycled by means of pipes 25 and 26 to alkylation tower 2. If it is desired to obtain substantially 2-methylbutene-2, the overhead product of 2-methylbutene-1 may be passed by means of pipes 23, 27, 25 and 26 to reactor 2. In either case a part of the recycle stream may be sent to the stripper 6 by means of pipes 25 and 28 or if desired pure product could be used for stripping via line 29. By these means it is possible to obtain substantially pure 2-methylbutene-1 or 2-methylbutene-2 or both in maximum yield and substantially pure form.

Example 1

Mixed meta, para-cresols (107.5 g.) with 1.22 mol per cent p-toluenesulfonic acid were alkylated in a bomb at 60° C. for 2 hours with a mixture of saturated and unsaturated hydrocarbons having 5 carbon atoms to the molecule and prepared by cracking. The product was stripped of unreacted C_5 hydrocarbons and then regenerated at

190–210° C. The C_5 product had a refractive index of 1.3851 corresponding to about 20% 2-methylbutene-1, and this product was further distilled to obtain 2-methylbutene-1 having a boiling point of 31.05 and an index of refraction of 1.3777 and another fraction having a refractive index of 1.3869 and a boiling point of 38.49° C.

Example 2

Pure (99+%) trimethylethylene (one mol) was used to alkylate mixed meta and para-cresols (2 mols) at 60° C. for 2 hours in the presence of 0.5 mol per cent p-toluenesulfonic acid. The product was stripped of traces of unreacted C_5 and then regenerated below 200° C. The C_5 product was distilled in a high-efficiency Podbielniak automatic still and found to be 99+% t-olefin composed of 18.4% 2-methylbutene-1 and 81.1% trimethylethylene.

Example 3

2.23 mols amylenes, 0.98 mol phenol and 0.0011 mol phenolsulfonic acid were heated for 2 hours at 60° C. in a bomb. The unreacted hydrocarbons were stripped off and the alkylated phenol decomposed by heat. The index of the recovered tertiary amylenes was 1.3848 which corresponds to an equilibrium mixture containing about 22% 2-methylbutene-1.

Conversely it may be shown that a feed containing no trimethylethylene but only 2-methylbutene-1 may be contacted with a phenol in the presence of a catalyst and upon regeneration of the resulting alkylated phenol at 200° C. an equilibrium mixture of trimethylethylene and 2-methylbutene-1 is obtained. This mixture may be fractionated, and pure trimethylethylene removed for use and the 2-methylbutene-1 recycled to the akylation step.

Although this invention deals specifically with tertiary amylenes it is recognized that isomers of higher tertiary olefin isomers may also be isolated in a similar manner; i. e. 2,3-dimethylbutene-2 (B. P. 73.3° C.) and 2,3-dimethylbutene-1 (B. P. 55.8° C.).

Also, the regenerations are not limited to the range of 190 to 200° C. but may be carried out at higher or lower temperatures under suitable pressures to give more or less 2-methylbutene-1 in the isomeric mixture of products. The maximum regeneration temperature will usually be fixed by the boiling point (at the regeneration pressure) of the alkylated phenol, and much lower temperatures may be used depending upon the nature and amount of the catalyst and the ease of dealkylation of the alkylated phenol.

This invention may also be applied in the alkylation and dealkylation of other aromatic compounds (hydrocarbons, etc.) containing a nuclear replaceable hydrogen and which are capable of alkylation by tertiary olefins.

I claim:

1. Method of preparing isomers of tertiary olefins which comprises contacting a tertiary olefin having at least 5 carbon atoms to the molecule with a phenol in the presence of an alkylating catalyst at a temperature of 0 to 100° C. to obtain an alkylated phenol, separating unreacted tertiary olefin from the alkylated phenol, heating the alkylated phenol to a temperature not substantially above the boiling point of the alkylated phenol at a regeneration pressure to obtain overhead a mixture of the isomers of the tertiary olefin, and separating individually the isomers of tertiary olefins retaining one as a product and recycling the undesired isomer of tertiary olefin to the tertiary olefin phenol mixture first made.

2. Method of preparing isomers of tertiary olefins which comprises contacting a tertiary olefin having at least 5 carbon atoms to the molecule with a phenol in the presence of an alkylating catalyst at a temperature of 0 to 100° C., separating unreacted tertiary olefin from a reaction product thereby obtained, heating the reaction product to a temperature of about 190–210° C. to distill over regenerated isomers of the tertiary olefin, separating individually the isomers of tertiary olefins, retaining one as a product, and recycling the undesired isomer of tertiary olefin to the tertiary olefin phenol mixture first made.

3. Method of preparing tertiary isomers of olefins which comprises contacting a tertiary olefin having 5 carbon atoms to the molecule with a cresol in the presence of p-toluene sulfonic acid at a temperature of about 60° C., separating unreacted tertiary olefin from an alkylated cresol thereby obtained, heating the alkylated cresol to a temperature of about 190–210° C. to distill over regenerated isomers of the tertiary olefin, separating individually the isomers of tertiary olefins, removing one isomer as a product and recycling other isomer to the tertiary olefin phenol mixture first made.

4. Method of preparing 2-methylbutene-1 which comprises alkylating a phenol with a tertiary olefin having 5 carbon atoms to the molecule, dealkylating resulting alkylated phenol to obtain a mixture of isomers of the tertiary olefin, separating individually first phenol and then 2-methylbutene-1 from the mixture, alkylating a phenol with the reisdual isomer, dealkylating the resulting alkylated phenol to obtain a mixture of isomers of the tertiary olefins and phenol and separating 2-methylbutene-1.

5. Method of preparing 2-methylbutene-1 according to claim 4 in which the dealkylation of the alkylated phenol is carried out in the presence of a nuclear condensation catalyst.

6. Method of preparing 2-methylbutene-2 which comprises alkylating a phenol with a tertiary olefin having 5 carbon atoms to the molecule, dealkylating resulting alkylated phenol to obtain a mixture of 2-methylbutene-1, 2-methylbutene-2 and phenol, separating the 2-methylbutene-2, alkylating a phenol with the 2-methylbutene-1, dealkylating the resulting alkylated phenol to obtain a mixture of 2-methylbutene-1, 2-methylbutene-2 and phenol, and separating the 2-methylbutene-2.

7. Method of preparing 2-methylbutene-2 according to claim 6 in which the alkylation temperature ranges from 0 to 100 and dealkylation temperature ranges from 190 to 210° C.

8. Method of preparing 2-methylbutene-2 according to claim 6 in which the dealkylation catalyst is benzenesulfonic acid.

9. Method of preparing isomers of tertiary olefins that are capable of existing in at least two isomeric forms which comprise contacting a phenol under alkylating conditions with a tertiary olefin having at least five carbon atoms to the molecule, heating the resulting alkylated phenol to a temperature and at a pressure sufficient to dealkylate it and to obtain an overhead mixture of isomers of the tertiary olefin and a residue of the phenol, separating the said olefin mixture into at least two portions, one of which containing a greater concentration of one of the isomers

than the other, withdrawing one of these portions and realkylating phenol with the other portion.

10. Method of preparing isomers of tertiary olefins which comprises contacting a phenol under alkylating conditions with a tertiary olefin having at least five carbon atoms to the molecule and capable of existing in at least two isomeric forms, separating the alkylated phenol from the unreacted tertiary olefin, heating the separated alkylated phenol to a temperature and pressure sufficient to dealkylate the separated alkylated phenol and to obtain an overhead mixture of isomers of the tertiary olefin and a residue of phenol, distilling the overhead mixture of isomers to obtain an overhead fraction of one of the isomers and a residual fraction of the other isomer, withdrawing one of these fractions as a product

and recontacting the other fraction with phenol under alkylating conditions.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,265,583	Stevens et al.	Dec. 9, 1941
2,290,602	Stevens et al.	July 21, 1942
2,290,603	Stevens et al.	July 21, 1942

OTHER REFERENCES

Wuyts, Chem. Zentral II, page 1006 (1912). (Patent Office Library.)