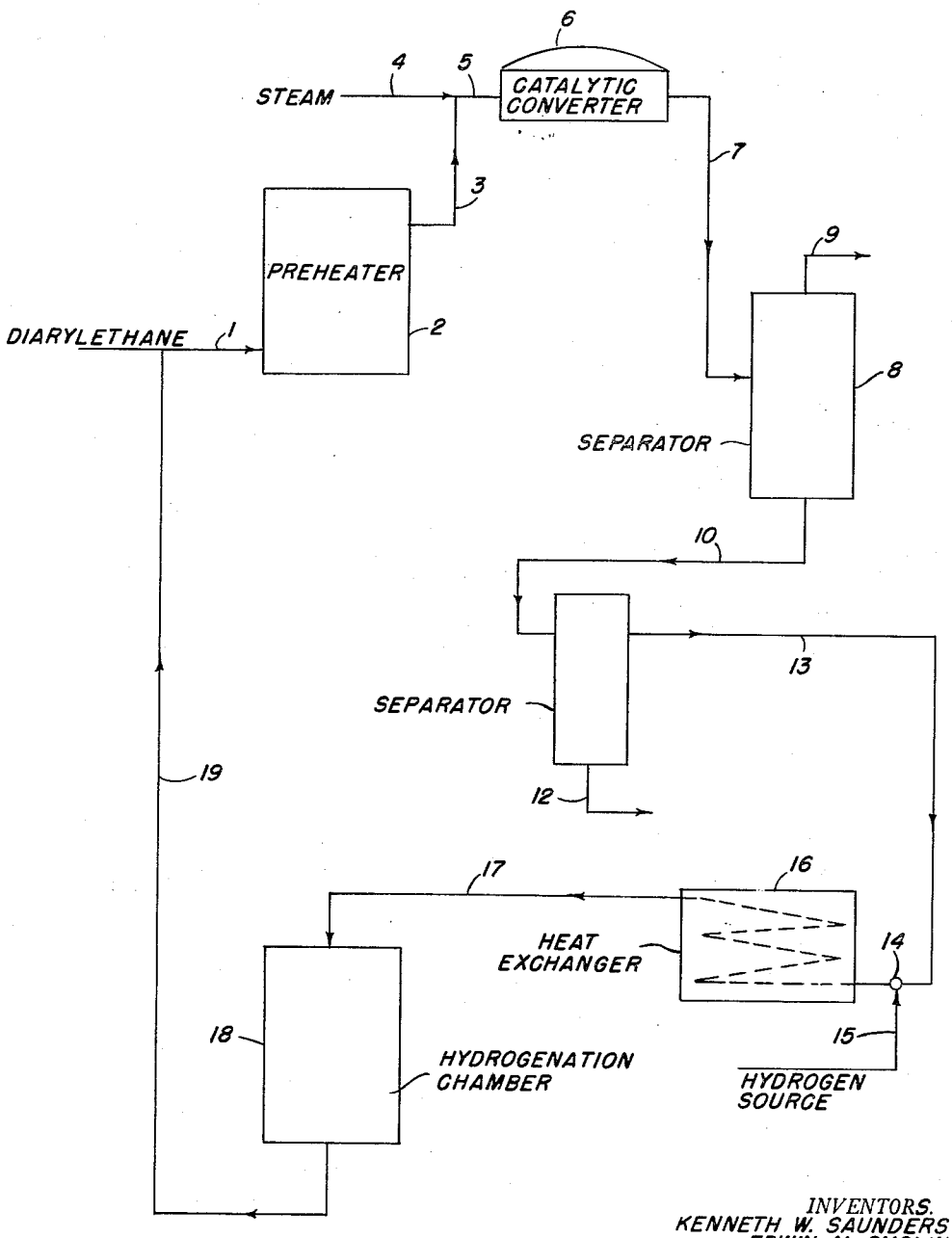
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PURIFICATION OF NON-CONVERTED MATERIAL IN THE CATALYTIC CRACKING OF DIARYLALKANES

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Fig. 1.



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Fig. 2.

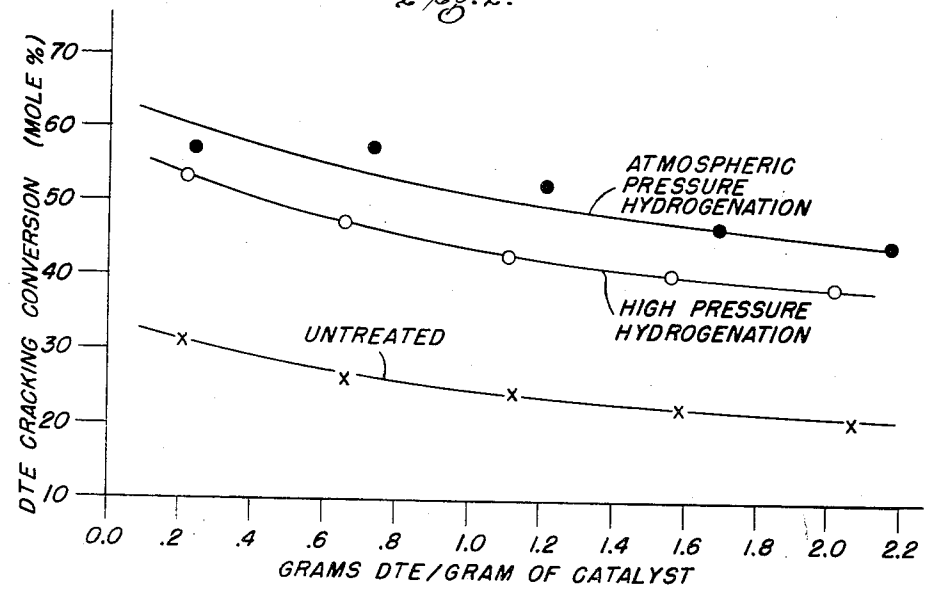
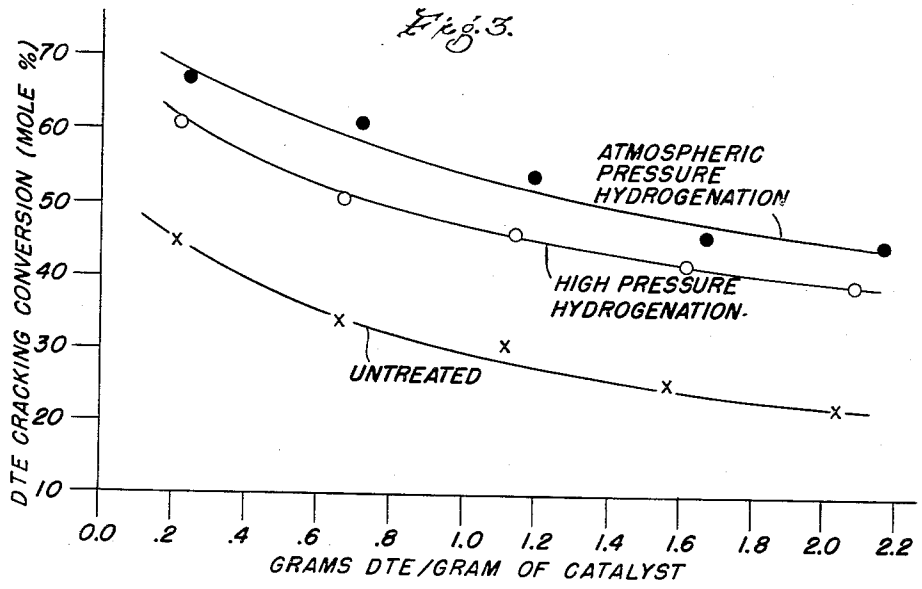


Fig. 3.



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PURIFICATION OF NON-CONVERTED MATERIAL IN THE CATALYTIC CRACKING OF DIARYLALKANES

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12 Claims. (Cl. 260—650)

This invention relates to the catalytic decomposition of unsymmetrical diarylalkanes. More particularly, this invention relates to a method of treating the accumulation of impurities formed in the non-converted recycle diarylalkane from the reaction product in the catalytic cracking of unsymmetrical diarylalkanes. Even more particularly, the invention resides in hydrogenating the non-converted material from diarylalkane catalytic decomposition reactions.

During the catalytic cracking of diarylalkanes to prepare polymerizable ring-substituted styrenes, a substantial accumulation of impurities forms in the recycled diarylalkanes. These impurities, comprising in substantial amount unsaturated diaryl compounds, are largely responsible for the progressively diminishing conversion obtained with diarylalkanes containing recycled diarylalkane. The build-up of these impurities during the recycling has been a major problem in the production of these polymerizable ring-substituted styrenes, such as methylstyrene from 1,1-ditolylethane. The separation of these "impurities," i. e., unsaturated diaryl compounds from the useable saturated diarylalkanes cannot be easily carried out by fractional distillation. Thus, the separation thereof has not heretofore been a practical means of treating recycle material.

According to the invention, we have found that by subjecting the recycled material to a hydrogenation reaction, a remarkable improvement in subsequent cracking conversion of recycled diarylalkane may be achieved. The conversion obtained following hydrogenation of the recycled material is substantially equivalent to that obtained when converting a compound comprising entirely fresh diarylalkane, i. e., no recycle material.

It is an object of this invention to increase the conversion of diarylalkane. More particularly, it is an object of the present invention to obtain an increased yield per pass of substituted styrene from the catalytic cracking of diarylalkanes. These and other objects are obtained by the hydrogenation of the unconverted diarylalkane prior to subjecting again the recycle to catalytic cracking.

Attempts have been made to remove the impurities, including unsaturated compounds, by various techniques, such as by distillation or chromatographic separation. However, all of these techniques have been largely unsuccessful for various reasons or they are only partially effective, i. e., the recovery of the diarylalkane is less than quantitative or the unsaturated diaryl compound, which is a source of the polymerizable material, is lost. These difficulties are overcome according to the invention by hydrogenating the unsaturated diaryl compound to the corresponding diarylalkane. The technique not only improves the conversion but also converts the harmful and non-useful unsaturated diaryl compound to the useful saturated diarylalkane necessary to produce the polymerizable monomer. In addition, the hydrogenation treatment converts to harmless compounds and improves the condition of other materials and impurities which are present in the recycle and which lower the conversion.

According to the invention, hydrogenation of the recycled non-converted diarylalkane from the catalytic cracking reaction may be conducted at atmospheric pressure, subatmospheric pressure, or at superatmospheric pressure. The hydrogenation is conducted in the presence of a suitable catalyst, such as for example, palladium on carbon or other suitable carrier or platinum on a suitable carrier.

In order to more fully illustrate the invention, the following examples are given by way of illustration and not as a limitation, except as expressed in the appended claims. Although the examples are described with reference to the treatment of 1,1-ditolylethane, other unsymmetrical diaryalkanes may be employed using the teaching of the invention.

HYDROGENATION OF RECYCLE DITOLYLETHANE

The hydrogenation of 1,1-ditolylethane under high pressure is conducted as follows: Each of the runs is carried out using about 2100 parts of ditolylethane with 50 parts of 5% palladium on carbon catalyst at a temperature of 25° C. to 35° C. and a hydrogen pressure of 1000–2000 p. s. i. The atmosphere pressure runs are carried out with the same catalyst and at the same temperature.

The reactions are carried out in a 3-necked vessel equipped with a stirrer and hydrogen inlet and outlet tubes. The ditolylethane recycle stream is flushed with hydrogen for 30 minutes before the catalyst is added. The catalyst is introduced as a slurry in ditolylethane and the hydrogen flow continues until there is no further evidence of heat evolution and the rate of hydrogen out of the flask equals the input rate. About a five-fold excess of hydrogen is used, although there is no evidence that such an excess is a requisite.

The changes in the physical properties of each of the runs as a result of hydrogenation and the hydrogen uptake are shown in Examples 1–10 of Table I.

Table I

HYDROGENATION OF DITOLYLETHANE EXAMPLES CONTAINING DITOLYLETHYLENE
[Refractive index (n_D^{25}) of ditolylethane=1.5620.]

Recycle Ditolylethane—Example	Palladium on Carbon Catalyst		Percent Ditolylethylene		n_D^{25}		Color	
	Percent Pd	Catalyst	Before	After	Before	After	Before	After
	H_2 Pressure: 1,000–2,000 p. s. i.							
1	10	25	2.9	0.0	1.5624	1.5616	Colorless	Colorless.
2	5	55	11.0	0.8	1.5706	1.5647	Orange	Light yellow.
3	5	50	25	0.2	1.5688	1.5607	Yellow	Very light yellow.
4	10	20	25	0.2				
5			25	0.2				
6	10	20	17.6	0.2			Yellow	Do.
7	10	20	16.4	0.2			do	Do.
8	10	20	20.7	0.2			do	Do.
	H_2 Pressure: Atmospheric							
9	10	25	25.0	0.2			do	Do.
10	10	25	5.0	0.1			do	Colorless.

In each case the hydrogen uptake is rapid and accompanied by some heat evolution. After a certain stage, hydrogen absorption ceases, which is indicative of the fact that the reaction is not complicated by partial hydrogenation of the aromatic rings.

The data in Table I show that the hydrogenation procedure essentially eliminates the unsaturation as determined by bromide-bromate titration, in all of the samples of recycled ditolylethane.

Hydrogenation tends to bring the refractive index (n_D^{25}) closer to the accepted value for pure ditolylethane ($1.5620 \pm .0005$).

It is observed that hydrogenation practically eliminates the color from all of the recycled ditolylethanes, although it is not definitely known whether this advantage results from the saturation of highly conjugated hydrocarbons or from the hydrogenation of colored oxygenated compounds.

CRACKING CONVERSIONS WITH HYDROGENATED 1,1-DITOLYLETHANE SAMPLES

The cracking conversions which are obtained with the various hydrogenated 1,1-ditolylethanes are presented in Table II and compared with the conversions obtained with the corresponding non-hydrogenated samples.

It is apparent that the cracking conversion of the hydrogenated sample of Example 1 is not significantly changed. This is an indication that the hydrogenation step does not affect the ditolylethane but only hydrogenates the unsaturated impurities.

It is evident that removal of unsaturated compounds, mainly ditolylethylene, from recycle ditolylethane has increased the conversion of the latter significantly.

Table II

EFFECT OF HYDROGENATION ON CONVERSION OF RECYCLE DITOLYLETHANE

Recycle Ditolylethane—Example	Unsaturation Calculated as Percent Ditolylethylene	Increase in Conversion of Ditolylethane to Methylstyrene after Hydrogenation (in absolute percent)
1	2.9	2
2	11.0	10–15
3	25.0	7–10
6	17.6	8–12
7	16.4	10–11
8	20.7	9–11
9	25.0	8–12

Figures 2 and 3 are further illustrative of the improved conversion through hydrogenation of the recycle material according to the invention. The curves in these figures illustrate the comparative conversion of material which has been hydrogenated either under atmospheric or under high pressure as against the conversion of non-hydrogenated or untreated recycle material.

Through the process of hydrogenation according to the invention, not only is the unsaturated diaryl compound converted to the corresponding diarylalkane but the deleterious effects of other olefins which may be found in the recycled diarylalkane and which have been found to be harmful are seemingly nullified. Hydrogenation also removes disadvantageous discoloration and compounds such as aldehydes, acids, quinones, peroxides, and the like, which have been found to have a bad effect on subsequent monomer production. Results obtained when the recycled material is hydrogenated produces a conversion having a value approximately equivalent to that obtained when converting a stream consisting entirely of fresh diarylalkane.

By reference to the flow sheet of Figure 1 of the accompanying drawing, the overall process which may be employed is illustrated. The flow sheet is in connection with the catalytic cracking of 1,1-ditolylethane to produce methylstyrene, but it will be understood that the procedure is equally applicable to the catalytic conversion of other unsymmetrical diarylalkanes.

In the drawing of Figure 1, ditolylethane is fed at **1** into the preheater **2** and is thereafter charged through **3** into a superheated steam diluent line **4**. The mixture is charged at **5** into the catalytic converter **6**. The catalytic conversion reaction products contain substantial amounts of methylstyrene, 1,1-ditolylethane, the corresponding unsaturated ditolylethane and various higher homologs, and tarry material, is fed through line **7** into the fractional distillation column 8. In this distillation column (or other suitable separation apparatus) the low boiling material including methylstyrene and toluene is withdrawn at **9** and further treated to separate the methylstyrene and toluene. The mixture comprising unconverted 1,1-ditolylethane, 1,1-ditolylethylene, and tarry residue is withdrawn at **10**. The mixture from line **10** is then introduced into the column **11**, where the tarry residue is removed at **12** and the 1,1-ditolylethane and 1,1-ditolylethylene is withdrawn at **13**. This mixture is then hydrogenated in a suitable manner. As shown, the material passing to the heated exchanger **16** is mixed at **14** with hydrogen fed through line **15**. The hydrogen-ditolylethane-ditolylethylene mixture leaving the heat exchanger passes through line **17** to the hydrogenation reaction chamber **18** where the unsaturated material in the mixture is hydrogenated and various other impurities are conditioned. Thereafter the hydrogenated ditolylethane may be charged through line **19** into the fresh ditolylethane feed at line **1**. The catalytic conversion of the recycle ditolylethane fractions may be conducted apart

from the conversion of the fresh material in which case the material from line 19 will be catalytic cracked in a separate catalytic converter (not shown).

Conventional valves, temperature controllers, flow regulators, and the like may be employed throughout the equipment in order to obtain optimum conditions for the process.

Diarylalkanes having at least two carbon atoms and having two aryl substituents attached to one of said carbon atoms are such as each of the 1,1-ditolylethanes, each of the 1,1-dixylylethanes, each of the 1,1-ditolylpropanes, each of the 2,2-ditolylpropanes, each of the 1,1-di-(monochlorophenyl)-ethanes, each of the 1,1-di-(dichlorophenyl)-ethanes, each of the 1,1-di-(dimethylaminophenyl)-ethanes, each of the 1,1-dinaphthylethanes, each of the 1,1-dixenylethanes, and the like, and their nuclear-substituted halogen, amino, and other derivatives. These substances containing tolyl, xylyl, xenyl, monochlorophenyl, and dichlorophenyl groups may be attached to the carbon atom of the paraffin chain at the ortho, meta, or para positions, and when two of these groups are present, they may be attached in the same or different positions. These compounds may be prepared, for example, by the reaction of acetylene or substituted acetylene and a mono- or di-alkyl substituted benzene in the presence of a suitable catalyst. Such compounds when catalytically decomposed yield ring- or nuclear-substituted styrenes which are useful in the production of thermoplastic polymeric materials. Another method that may be employed in the production of diarylalkanes is such as the condensing of an aryl compound with a saturated aliphatic organic compound having a carbonyl group and at least two carbon atoms, e. g., aldehydes and ketones, in the presence of a suitable catalyst, such as hydrogen fluoride or sulfuric acid.

The catalytic conversion of these paraffins having at least two carbon atoms and having two aryl substituents attached to one of said carbon atoms is well known. U. S. Patent Nos. 2,422,163; 2,422,164; and 2,422,165 disclose various catalysts that may be employed for such decomposition. Upon partial decomposition of the substituted paraffins, a plurality of organic compounds is obtained. The mixture contains undecomposed substituted paraffin, vinyl-substituted aryl compounds and alkyl-substituted compounds. When a 1,1-diarylalkane, such as 1,1-ditolylethane is synthesized from acetylene and toluene and is then partially catalytically converted, the resulting mixtures contain 1,1-ditolylethane, methylstyrene, toluene, a small percentage of ethyltoluene, 1,1-ditolylethylene, and tarry material. In the event that a 1,1-dixylylethane is synthesized and converted, the resulting mixture contains undecomposed 1,1-dixylylethane, dimethylstyrene, xylene, a small amount of ethylxylene, 1,1-dixylylethylene, and tarry material. By the process of our invention, a more effective utilization of the organic compounds contained in the mixtures is possible.

The partial catalytic decomposition of the substituted paraffins may be carried out at temperatures varying from about 350° C. up to about 600° C., or even higher in some cases, in the presence of a suitable decomposition catalyst. Inasmuch as temperatures above about 500° C. start to cause some pyrolysis loss, it is important to employ a short time of contact of the substituted paraffins with the catalyst when temperatures in the neighborhood of 500° C. are used. Any material which is volatile, which does not react with the diaryl-substituted paraffin, and which does not react with the products formed by the decomposition of said paraffin may be used as a diluent during the partial catalytic decomposition. Among these, some examples are water, hydrocarbons, such as benzene and toluene, the fixed gases, such as nitrogen and carbon dioxide, and the like. Water vapor, i. e., superheated steam, is the preferred diluent, inasmuch as it may be readily condensed and therefore separated from the products of the reaction, whereas the fixed gases or the hydrocarbons are somewhat more difficult to separate. The molar ratio of diluent to the diaryl-substituted aliphatic compound in the feed to the catalyst during decomposition is preferably between about 5:1 and 200:1 or more.

It will be apparent that various modifications are possible within the scope of the invention and that the enumeration of specific details is not intended as a limitation of the invention, except as defined in the appended claims.

We claim:

1. In the method of catalytically cracking unsymmetrical diarylalkanes having at least two carbon atoms and having the two aryl substituents attached to one of said carbon atoms to produce ring-substituted polymerizable compounds wherein the substituent is selected from the group consisting of lower alkyl radicals having 1–4 carbon atoms and halogen atoms, the step comprising hydrogenating the non-converted material from the cracking reaction containing unsaturated aryl compound and other impurities and thereafter catalytically cracking said hydrogenated material.

2. In a method of producing ring-substituted styrene compounds by the catalytic cracking of unsymmetrical diaryl-ethanes, wherein the substituent is selected from the group consisting of lower alkyl radicals having from 1 to 4 carbon atoms and halogen, the step comprising hydrogenating the uncracked material from the cracking reaction containing unsaturated diarylethane and other impurities and thereafter catalytically converting said hydrogenated material.

3. In a method of producing methylstyrene by the catalytic cracking of 1,1-ditolylethane, the step comprising hydrogenating the uncracked material from the cracking reaction containing ditolylethylene and other impurities and thereafter catalytically cracking said hydrogenated material.

4. In a method of producing dimethylstyrene by the catalytic cracking of 1,1-dixylylethane, the step comprising hydrogenating the uncracked material from the cracking reaction containing dixylylethylene and other impurities and thereafter catalytically cracking said hydrogenated material.

5. In a method of producing chlorostyrene by the catalytic cracking of 1,1-bis(chlorophenyl)ethane, the step comprising hydrogenating the uncracked material from the cracking reaction containing 1,1-bis(chlorophenyl)-ethylene and other impurities and thereafter catalytically cracking said hydrogenated material.

6. In a method of producing ring-substituted styrene compounds by the catalytic cracking of unsymmetrical diarylalkanes, wherein the substituent is selected from the group consisting of lower alkyl radicals having from 1–4 carbon atoms and halogen, and wherein the uncracked diarylethane is recycled, the step comprising hydrogenating the recycled material containing unsaturated diarylalkane and other impurities and thereafter catalytically cracking said hydrogenated recycle in admixture with fresh diarylalkane feed and diluent.

7. In a method of producing ring-substituted styrene compounds by the catalytic cracking of 1,1-diarylethanes, wherein the substituent is selected from the group consisting of lower alkyl radicals having from 1–4 carbon atoms and halogen, and wherein the uncracked diarylethane is recycled, the step comprising hydrogenating the recycled material containing unsaturated diarylethane and other impurities and thereafter catalytically cracking said hydrogenated recycle in admixture with fresh 1,1-diarylethane feed and diluent.

8. In a method of producing methylstyrene by the catalytic cracking of 1,1-ditolylethane, wherein the uncracked ditolylethane is recycled, the step comprising hydrogenating the recycled material containing ditolylethylene and other impurities and thereafter catalytically cracking said hydrogenated recycle in admixture with fresh ditolylethane feed and diluent.

9. The method of claim 8 wherein the diluent is superheated steam.

10. In a method of producing dimethylstyrenes by the catalytic cracking of 1,1-dixylylethane, wherein the uncracked dixylylethane is recycled, the step comprising hydrogenating the recycled material containing dixylylethylene and other impurities and thereafter catalytically cracking said hydrogenated recycle in admixture with fresh dixylylethane feed and diluent.

11. The method of claim 9 wherein the diluent is superheated steam.

12. In a method of producing chlorostyrene by the catalytic cracking of 1,1-bis(chlorophenyl)ethane, wherein the uncracked diarylethane is recycled, the step comprising hydrogenating the recycled material containing 1,1-bis(chlorophenyl)ethylene and other impurities and thereafter catalytically cracking said hydrogenated recycle in admixture with fresh 1,1-bis(chlorophenyl)ethane feed and diluent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,106,013	Ocon	Jan. 18, 1938
2,422,166	Dixon et al.	June 10, 1947

OTHER REFERENCES

Wooster et al.: Jour. Amer. Chem. Soc., vol. 56, May 1934, pp. 1133–36.