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DEALKYLATION PROCESS

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This invention relates to the dealkylation of alkyl cyclic compounds. More particularly, the invention relates to the production of aromatic compounds of desired molecular weight or boiling point by a process of dealkylating alkyl aromatic compounds of higher molecular weight or boiling point.

While alkyl aromatic compounds may be used for many purposes, either as such or as starting material for producing other compounds, one of the more important uses is that of blending material for motor fuels, due to the high anti-knock qualities of the alkyl aromatic compounds. This latter use of alkylated aromatic compounds is especially important for motor fuels of high compression type engines as, for example, the engines designed for aviation. Since the alkylated benzenes must be of the gasoline boiling range in order to be blended with the motor fuels, various processes have been proposed to produce high yields of alkyl aromatic compounds which are within the desired boiling range.

For the most part prior processes of preparing particular alkyl aromatic compounds partake of chemical synthesis reactions in which aromatic compounds such as benzene are condensed with appropriate aliphatic compounds. It has also been proposed in the past to reform polyalkyl aromatic compounds as, for instance, natural occurring alkyl aromatics of coal tar, such as xylene, or by reforming polyalkyl aromatic products produced during alkylating processes, such as noted above. These prior processes of reforming polyalkyl aromatic compounds have been carried out either at relatively low temperatures as, for instance, temperatures below about 300° F. and in the presence of catalysts, such as aluminum chloride or sulfuric acid, or the processes have involved merely a cracking operation at high temperatures in the absence of catalysts. While it is true these prior processes have brought about dealkylation of polyalkylated aromatics to a certain extent, they are subject to many disadvantages.

The most serious objection to dealkylation processes at low temperatures in the presence of catalysts, such as aluminum chloride is that it is a very slow process which lasts many hours or days in order to form a substantial yield of low boiling aromatics. While the inordinate amount of time required for such low temperature processes is the most serious disadvantage, another objection to their use is that of low yield of low boiling point aromatic compounds and especially when treating alkyl aromatics containing

relatively long chain aliphatic radicals. Moreover, increases of temperature in this dealkylation process result in the formation of sludge and tarry materials. These catalytic processes conducted at low temperatures are also open to other objections. For instance, such processes when employing the usual low temperature-reactive catalysts, such as aluminum chloride and sulfuric acid consume a relatively high quantity of catalytic material or, if the catalyst is not entirely consumed, a complicated and costly process of regeneration is required. Moreover, many of these catalytic materials are corrosive to the materials of construction normally used and introduce this as well as other operating difficulties.

The most serious objection to the prior processes which involve a non-catalytic cracking operation is that of low yield of low boiling aromatics. However, in addition to this disadvantage, this type of process also forms a considerable amount of heavy residua of the nature of coke and asphaltic material.

It is an object of this invention to produce an efficient process for effecting the dealkylation of mono- and polyalkyl cyclic compounds to produce aromatic compounds of lower boiling point.

A more specific object of this invention is to provide an efficient process for effecting the dealkylation of mono- and polyalkylated aromatic compounds of relatively high boiling point to produce substantial yields of alkyl aromatic compounds of motor fuel boiling point.

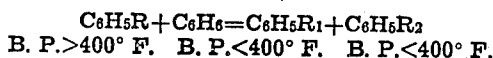
Another object of this invention is to provide an efficient process for effecting the dealkylation of mono- and polyalkylated compounds of relatively high boiling point to produce substantial yields of alkyl aromatic compounds of lower boiling point and which may be carried out in a relatively short time as compared to prior catalytic processes afforded by the prior art.

Our invention is based upon the discovery that alkyl cyclic compounds may be treated with benzene at relatively high temperatures of the nature herein disclosed in the presence of suitable catalysts to produce substantial yields of valuable aromatic compounds of lower molecular weight.

A remarkable feature of the present discovery is the fact that an almost complete recovery of the benzene charged to the reaction is obtained. While, in some cases, a small amount of this benzene is consumed, the yield of alkyl aromatic compounds formed is correspondingly greater.

The complete recovery of benzene in the destructive dealkylation of alkyl cyclic compounds is quite unexpected. In the case of high molec-

ular weight alkyl benzenes, the destructive dealkylation by benzene may be according to the general equation wherein the alkyl radical R is broken down into smaller radicals R₁ and R₂:



A partial dealkylation of alkyl aromatics formed in the initial stages of the process completely to benzene in the latter stages of the reaction may explain the total or almost total recovery of benzene. If other alkyl aromatic compounds are being treated they are probably dealkylated in a similar manner. If alkyl naphthenic hydrocarbons are treated, it is quite probable that they first undergo a dehydrogenation reaction to form alkyl aromatic hydrocarbons and then the alkyl aromatic hydrocarbons thus formed undergo dealkylation reactions of the type above illustrated.

The amount of benzene that may be used may vary considerably. From a practical standpoint we have found a ratio of benzene to material treated of about 1/2 volume to 2 volumes of benzene to 1 volume of material treated usually gives proper proportioning for obtaining our desired results. It is to be understood, however, the invention is not limited to the above ratio but rather contemplates the broad use of benzene in any amount which gives our novel results.

In addition to treating with benzene, we have carried out the destructive dealkylation of alkyl cyclic compounds by treating with other aromatic hydrocarbons instead of benzene, for example, naphthalene, alpha methyl naphthalene and alkyl naphthalenes. The yields of low boiling alkylated benzenes in these experiments are much lower than with benzene. This indicates that the capacity of naphthalene for alkylation is much less than that of benzene at these temperatures which might be expected, due to the relatively higher thermal stability of alkylated benzenes.

The alkyl cyclic compounds which may be treated in accordance with our process include not only mono- and poly-alkylated benzenes, but also mono- and poly-alkylated naphthalenes and other poly-cyclic alkyl aromatic compounds as well as various mono- and poly-cyclic alkylated naphthenes. While these compounds may be obtained from any suitable supply, a convenient source that might be mentioned by way of example is the heavier portion of the product of an alkylation process for alkylating aromatic material wherein the heavier portion comprises aromatic material which has been alkylated beyond the desired degree.

Thus these alkyl aromatic hydrocarbons boiling for example, above 400-435° F. are easily transformed into lower molecular weight aromatics boiling up to 400° F. or only 300° F. by destructive dealkylation under the conditions of our process, giving a yield of lower boiling aromatics which is much higher than that produced by the known processes of low temperature dealkylation or the usual cracking process.

The catalysts with which this invention is concerned are those which are commonly known as clay type. In addition to the various clays themselves and the various activated clays, there are numerous other porous refractory adsorptive materials of similar nature and of neutral character which may be used and come under the common designation of clay-type catalysts, for example, fuller's earth, pumice and granular diatomaceous

earth. Furthermore, it is to be understood that these various clay type catalysts which have other suitable catalytic material impregnated therein or thereon or otherwise conjoined for service may also be used.

Since the dealkylation reaction together with the attendant cracking reactions which are present at the temperature herein disclosed bring about a gradual poisoning or deterioration of the catalyst by the deposition of carbon and carbonaceous impurities thereon, it is well to use a clay which is possessed of sufficient refractory nature so that it may be regenerated in situ by burning. In fact, some of the clay catalysts used by us have been regenerated a great number of times and are still quite satisfactory. Because of the ease with which the clay type catalyst may be regenerated, they afford a substantial advantage in their use. It is also well to use clay particles of such physical nature with respect to size and dimension that they may be effectively packed together in a catalytic mass and yet, at the same time, present a sufficient cross-sectional area of flow that the reactants may have a ready passage therethrough, as well as a suitable exposure of catalytic material to reactants. A convenient and efficient form for the catalyst is small granules, rods or cylinders.

The use of clay catalyst has many distinct advantages in addition to those already named. For instance, the clay is not corrosive to the normal apparatus as are many catalysts and, furthermore, there is relatively small consumption of the catalyst during operation. However, the most important advantage in the use of clay type catalyst is that under operable conditions there is obtained such markedly improved results as to increase yield and decrease time of operation.

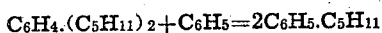
The temperature employed in our process should be upwards of about 800° F. It is desirable to maintain the temperature between about 800 and about 900° F. unless the process is to be operated in a continuous manner when temperatures up to about 1050° F. may be used.

While the process should be carried out under super-atmospheric pressures in batch operation, there is a wide range in the pressures that may be used. In the preferred embodiment of our invention for batch operation, we employ pressures between about 1000 and 2500 pounds per square inch. It is to be understood the process may be carried out at other pressures as, for instance, in continuous operation the pressure might be much lower than 1000 pounds per square inch, in fact for continuous operation atmospheric pressure or pressures of only a few atmospheres are preferred. As a whole, the operations at these different pressures give very close results relative to the yields and properties of products, recovery of benzene etc.

Under the conditions of our process the destructive dealkylation usually takes place in about forty minutes for batch operation at 900° F., for example, which represents a remarkable improvement over prior processes which require far greater lengths of time and do not give the high yields of low boiling aromatic compounds produced by our process. In continuous operation at 1000° F., for example, the time of reaction is usually around one minute.

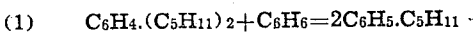
In order to further point out the differences between our process and the processes of low temperature catalytic reactions heretofore enjoyed by the art, we may discuss the reactions involved. For example, when di-amyl benzene is deal-

kylated at low temperature, the following reaction takes place:

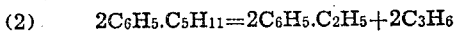


Thus, according to this process, as may be observed, di-amyl benzene is converted into two molecules of amyl benzene which has a boiling point of 401° F., which is barely within the upper limits acceptable for ordinary motor fuel and which is unacceptable for use in lighter gasolines as, for example, aviation gasoline.

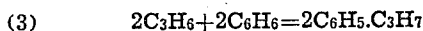
In contrast to the above reaction, the reactions of our process when treating the same di-amyl benzene are of the following nature:



and, for instance,



and similar equations for the formation of other alkyl benzenes. If the process is carried out under high pressure, secondary reactions of alkylation are possible, as, for instance,



Accordingly, in our process the final products obtained are low boiling alkyl benzenes which may be used even in the low boiling types of gasoline, such as aviation gasoline. These differences in the type of reaction encountered are even more striking when the aliphatic radicals of the alkyl aromatic compounds have a greater number of carbon atoms. However it is not only the final product that establishes a striking difference over prior low-temperature catalytic processes, but, furthermore, the very substantial decrease in reaction time is of particular importance, especially from a practical standpoint.

It is also to be noted that the destructive dealkylation of alkyl benzenes to benzene progresses more and more with increasing reaction time. Accordingly, by suitably extending the time of reaction more than 100% benzene (based on the amount of benzene charged to the reaction) may be recovered from the final products due to a complete dealkylation of a part of the alkyl aromatics. In other words, under the dealkylating action of clay, alkyl benzenes may be com-

the combined weight of benzene and alkyl aromatics) and dealkylated according to our process. The pressure used in the cracking process was 900 lbs./sq. in. and in our dealkylation process the pressure was 2200 lbs./sq. in. Otherwise the conditions of the two processes were the same, i. e., the temperature was 900° F. and the reaction time was 40 minutes. The following results were obtained from these two processes:

	Cracking	Catalytic dealkylation
Light ends and gas.....	4%-----	9%.
Dealkylated aromatics boiling 95-150° C.....	25%—0.866 sp. gr.	62%—0.866 sp. gr.
Recycling material boiling 150-210° C.....	43%—0.872 sp. gr.	23%—0.874 sp. gr.
Residuum.....	23%—1.04 sp. gr.	22%—1.03 sp. gr.
Carbon and insoluble asphaltic material.....	5%-----	None.
Total.....	100%-----	116%.

It is to be noted that by our process there was produced 62% of dealkylated aromatic boiling in the desired range of 95° to 150° C., while only 25% of such compounds were produced by the cracking process. Moreover, the cracking process produced 5% of carbon and insoluble asphaltic material whereas our process produced none. It is also to be noted that the total amount of all recovered products in our catalytic dealkylation process was 116%. In other words, 8% of the benzene charged was consumed in the process of dealkylation.

Further tests were carried out comparing the present process with that of cracking and also cracking in the presence of clay without benzene and cracking in the presence of benzene without clay. In these experiments alkylated aromatic hydrocarbons boiling in the range of 150 to 250° C. (obtained by alkylating benzene with olefines) were employed as a material for the destructive dealkylation. The destructive dealkylation was carried out at a temperature of 900° F. (482° C.) under a pressure of about 1,000 pounds per square inch for a time of 40 minutes. The relative amount of benzene used was two volumes per one volume of material to be alkylated. These experiments gave the following results:

No.	Clay	Benzene	Recovery of benzene	Products formed					
				Light ends	Toluene in 78°-95° fraction	Alkyl arom. boiling 95°-150° C.	Recycling stock 150°-210° C.	Residuum	Coke
	Per cent	Volume	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	
1-----	None	None	-----	3.5	(1.0) (x)	29.0	49.7	11.8	5% (xx).
2-----	15	None	-----	2.2	(7.8) (x)	24.6	41.9	23.4	Very small.
3-----	None	2	99	5.4	4.3	23.6	47.0	22.1	None.
4-----	15	2	99	4.0	5.6	42.0	23.0	16.8	Do.
5-----	30	2	90	2.3	7.8	59.9	22.8	22.0	Do.

pletely dealkylated to benzene even at the temperatures of our process.

In order to more clearly illustrate the invention and to contrast the improved results obtained thereby over the results obtained by prior cracking processes, the following experiments are cited wherein two portions of alkyl aromatic compounds falling in the range of 150 to 250° C. boiling point and of specific gravity 0.865 were dealkylated. One portion of the alkyl aromatic compounds was dealkylated by a usual cracking process and the other portion of the alkyl aromatic compounds was treated with two volumes of benzene and 30% of activated clay, (based on

The above table clearly shows the remarkably improved results obtained in Experiments 4 and 5 by our process of operation. In Experiment 4 of the above table giving a yield of 42% of the desired compounds, the recovery of benzene was practically complete and in Experiment 5 (with a yield of 60% of the desired alkyl aromatic compounds) a considerable amount of benzene was consumed resulting in a corresponding increase in the yield of alkyl benzenes. In order to show that under the dealkylating action of clay and the temperatures of our process, alkyl benzenes may be completely dealkylated to benzene, a further experiment of dealkylation of

alkyl benzenes was carried out under the same conditions as in Experiment 4 of the above table but with a longer time of reaction, all other conditions being identical. The following results were obtained:

zene to 1 volume of alkyl aromatics in contact with an activated clay dealkylation catalyst at a temperature between about 800° F. and about 900° F. and under a pressure between about 1000 and about 2500 lbs. per square inch, heating said mix-

*Destructive dealkylation of high boiling aromatics at 900° F.,
15% clay, 2 volumes of benzene per 1 volume of aromatics*

No.	Time, mins.	Recovery of benzene	Products formed				
			Light ends	Toluene in 78-95° fraction	Alkyl arom. boiling 95°-150° C.	Recycling stock 150°-210° C.	Residuum
4.....	40	Percent 99	Percent 4.0	Percent 5.6	Percent 42.0	Percent 23.0	Percent 16.8
6.....	58	104	10.4	4.5	36.2	24.3	18.3

From this last table it is seen that with a longer period of reaction 104% of benzene is recovered.

We claim:

1. The process of producing relatively low molecular weight alkyl aromatic compounds from alkyl aromatic compounds of higher molecular weight which comprises continuously passing a mixture of benzene and said higher molecular weight alkyl aromatic compounds in the ratio of ½ to 2 volumes of benzene to 1 volume of alkyl aromatics through a heating zone in contact with an activated clay dealkylation catalyst at a temperature between about 800° F. and about 1050° F. and under substantially atmospheric pressure, said mixture being kept in said heating zone for a sufficient length of time to produce the desired alkyl aromatic compounds, withdrawing the treated mixture, separating the desired low molecular weight alkyl aromatic compounds and recovering at least substantially all the admixed benzene.

2. The process of producing alkyl aromatic compounds boiling within the gasoline boiling range from alkyl aromatic compounds of higher boiling range which comprises continuously passing a mixture of benzene and said higher boiling alkyl aromatic compounds through a heating zone in contact with an activated clay dealkylation catalyst at a temperature between about 800° F. and about 1050° F. and under substantially atmospheric pressure, said mixture being kept in said heating zone for a sufficient length of time to produce the desired alkyl aromatic compounds.

3. The process of producing relatively low molecular weight alkyl aromatic compounds from alkyl aromatic compounds of higher molecular weight which comprises continuously passing a mixture of benzene and said higher molecular weight alkyl aromatic compounds through a heating zone containing a dealkylation catalyst comprising an association of silicon oxide and aluminum oxide and maintained at a temperature between about 800° F. and about 1050° F. and under substantially atmospheric pressure, said mixture being kept in said heating zone for a sufficient length of time to produce the desired alkyl aromatic compounds, withdrawing treated mixture and recovering at least substantially all the benzene admixed therewith.

4. The process of producing alkyl aromatic compounds boiling within the gasoline boiling range from alkyl aromatic compounds of higher boiling range which comprises heating a batch mixture of benzene and said higher boiling alkyl aromatics in the ratio of ½ to 2 volumes of ben-

zene to 1 volume of alkyl aromatic compounds, separating alkyl aromatic compounds of gasoline boiling range from the treated mixture and recovering at least substantially the total quantity of admixed benzene.

5. The process of producing alkyl aromatic compounds boiling within the gasoline boiling range from alkyl aromatic compounds of higher boiling range which comprises heating a batch mixture of benzene and said higher boiling alkyl aromatic compounds in the presence of an activated clay dealkylation catalyst at a temperature between about 800° F. and about 900° F. and under a pressure between about 1000 and about 2500 lbs. per square inch, said mixture being heated for a sufficient length of time to produce the desired alkyl aromatic compounds.

6. The process of producing alkyl aromatic compounds boiling in the gasoline boiling range from alkyl aromatic compounds of higher boiling range which comprises treating said latter alkyl aromatic compounds with benzene at a temperature between about 800° F. and about 1050° F. in the presence of an activated clay dealkylation catalyst.

7. The process of producing aromatic compounds of relatively low molecular weight from alkyl aromatic compounds of higher molecular weight which comprises reacting a mixture of said alkyl aromatic compounds and benzene in the presence of a dealkylation catalyst comprising an association of silicon oxide and aluminum oxide at a temperature between about 800° F. and about 900° F. and a pressure between about 1000 lbs./sq. in. and about 2500 lbs./sq. in.

8. The process of producing aromatic compounds of relatively low molecular weight from alkyl aromatic compounds of higher molecular weight which comprises treating said alkyl aromatic compounds with benzene at temperatures between about 800° F. and about 1050° F. in the presence of a dealkylation catalyst comprising an association of silicon oxide and aluminum oxide.

9. The process of producing relatively low molecular weight aromatic compounds from alkyl cyclic compounds of higher molecular weight which comprises treating said alkyl cyclic compounds with benzene at a temperature between about 800° F. and about 1050° F. in the presence of a dealkylation catalyst comprising an association of silicon oxide and aluminum oxide.

10. In a process for producing alkyl aromatic compounds boiling in the gasoline boiling range from alkyl cyclic compounds of higher boiling

range, the improvement which comprises treating said higher boiling alkyl cyclic compounds with benzene in the presence of an activated clay dealkylation catalyst and at a temperature between about 800° F. and about 1050° F.

11. In a process for producing aromatic compounds of relatively low molecular weight from alkyl cyclic compounds of higher molecular weight, the improvement which comprises treating said higher molecular weight alkyl cyclic compounds with benzene in the presence of a dealkylation catalyst comprising an association of silicon oxide and aluminum oxide and at a temperature between about 800° F. and about 1050° F., and recovering at least substantially all the benzene used to treat said alkyl cyclic compounds.

12. The process of producing aromatic compounds of relatively low molecular weight from alkyl cyclic compounds of higher molecular weight which comprises treating said alkyl cyclic

compounds with a substantially unsaturated aromatic compound containing not more than two rings of relatively low molecular weight at a temperature between about 800° F. and about 1050° F. in the presence of a dealkylation catalyst comprising an association of silicon oxide and aluminum oxide.

13. The process of dealkylating alkyl cyclic compounds which comprises treating said alkyl cyclic compounds with benzene at temperatures between about 800° F. and about 1050° F. in the presence of a clay dealkylation catalyst.

14. The process of dealkylating alkyl aromatic compounds which comprises treating said alkyl aromatic compounds with benzene at temperatures between about 800° F. and about 1050° F. in the presence of a clay dealkylation catalyst.

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