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CATALYTIC OIL CRACKING

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This invention relates to an improved process for the catalytic cracking of hydrocarbon oils to produce a high yield of gasoline motor fuel of high octane rating. In another aspect it relates to a process for the catalytic cracking of hydrocarbon oils in which the yield of gaseous by-products is low. In still another aspect it relates to such a process in which the amount of carbon deposition is low.

In the production of gasoline motor fuel from petroleum, a small amount may be obtained by simple fractionation. Since gasoline motor fuel is the product in greatest demand, efforts are being constantly made to devise methods or processes to produce this gasoline motor fuel in greater quantities. The processes presently giving best results rely on the conversion of higher boiling hydrocarbon oils into low-boiling gasoline motor fuels in a system employing a catalyst in the conversion zone. This catalyst may be used in a fixed bed or a fluidized system. The search for improved catalysts is being pushed constantly and probably will never be ended.

Since the cracking reactions and catalyst regeneration are carried out at fairly high temperatures, a good catalyst must be able to withstand exposure to high temperatures without serious impairment of efficiency. The process must allow a high throughput of high-boiling point oil and return a high yield of high octane gasoline. The amount of dry gas (propane and lighter hydrocarbons) and butanes formed should be low. As carbon from the cracking builds up on the catalyst, the catalytic activity drops and the catalyst must be taken out of service for regeneration when the activity drops to a certain predetermined level. Therefore, it is desirable that the rate of carbon deposition be as low as is consistent with economical operation of the process.

The prior art teaches the use of catalysts comprising synthetic aluminas impregnated with tin oxide and even bauxite impregnated with tin oxide, but with respect to the latter, the teaching is that bauxite impregnated with tin oxide is an inferior catalyst and its use is therefore condemned and has never been used in practice.

The principal object of my invention is to provide an improved process for the catalytic conversion of high-boiling petroleum oils into high octane gasoline motor fuels at a high yield

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through the use of the catalyst comprising bauxite supporting a minor proportion of tin oxide as a promoter.

Another object of my invention is to provide a process for the catalytic conversion of high-boiling point petroleum oils into high octane gasoline motor fuels at a high yield and with a minimum amount of dry gas and butane formation.

Another object of my invention is to provide a process for the catalytic conversion of high-boiling point petroleum oils into high octane gasoline motor fuels at a high yield and with a minimum amount of carbon deposition.

Another object of my invention is to provide a process for the catalytic conversion of high-boiling point petroleum oils into high octane gasoline motor fuels, in which process, the catalyst is maintained at high activity and high efficiency for longer periods.

Numerous other objects and advantages of my invention will be apparent to those skilled in the art upon reading the following specification and the accompanying claims.

Operations

My invention is an improved process for the catalytic conversion of high-boiling point petroleum oils into high octane gasoline motor fuel wherein use is made of an improved catalytic mass comprising calcined bauxite, impregnated with a minor amount of tin oxide.

In its operation, the high-boiling point oil is substantially vaporized in a preheater, passed into a catalytic reactor where it is contacted with the catalyst for the desired time, and then passed into a conventional fractionating and separating system for the recovery of the gasoline.

Before the petroleum oil is introduced into the high temperature section of the preheater, I prefer to dilute it with about 60 lbs. of steam per barrel of oil. Any other inert diluent gas may be used or this dilution may be omitted entirely. The charge is vaporized and superheated with as little thermal decomposition as possible to a temperature in the range of 850–1100° F. A pressure of 10–300 pounds per square inch at the preheater outlet is preferred.

The vaporized petroleum oil is passed from the preheater into the catalytic reactor where it contacts the catalytic mass at a space velocity of

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from 0.1 to 10 liquid volumes of petroleum oil per volume of catalytic mass per hour. The amount of conversion is partially controlled by the length of time the oil is exposed to the catalyst. However, if the velocity is low, the process is uneconomical because the total product will be low. If the space velocity is too high, the per cent conversion is low. I prefer a space velocity of about 0.5 to 2 liquid volumes of oil per volume of catalyst per hour. I prefer to use a top bed catalyst temperature of 950-1000° F. and a catalyst case pressure of 10-95 pounds per square inch. The pressure may be varied over a fairly wide range with very little effect on the conversion yield.

For my catalyst I prefer to use a high grade bauxite whose iron content is below 3 per cent which has been impregnated with tin oxide as a promoter. The tin oxide content may vary between 0.1 and 5 weight per cent of the total mass. I prefer to use from 0.5 to 2 per cent of tin oxide.

The effluent gases from the catalytic reactor are led into a separator where the gasoline motor fuel, dry gas, and butanes are removed. The high-boiling fraction may be recycled through the system by introducing it back into the preheater along with the new oil. The following examples serve to illustrate further the advantages of my invention.

All pressures used in this specification are expressed as pounds per square inch gauge.

EXAMPLE I

In the preparation of my catalyst a sample of bauxite having an iron content below 3 per cent and ground to particle size of 8-14 mesh was calcined at 900° F. until the water content was approximately 5 per cent so that it would absorb the SnCl_4 solution more readily.

To a 250 gram portion was added 250 ml. of an aqueous solution containing 25.7 grams of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and the mass was allowed to stand for 1 hour. The gel-like mass that formed was soaked in 250 ml. of 1N NH_4OH for 1 hour. The excess liquid was then drained off and the catalyst mass was washed continuously for 4 hours with distilled water and then dried at 120° F. for 36 hours and finally at 896° F. for 20 hours.

The catalyst containing the promoter and the untreated bauxite were then heated to 1500° F. for 500 hours to kill the initial high activity common to such catalysts and attain the activity that would be expected after several days use. It was determined by calculation that the content of tin oxide was 1.5 per cent.

EXAMPLE II

Two runs were made to compare the catalytic effect of the sample of promoted bauxite prepared in Example I with the same bauxite minus the promoter.

The tests were carried out by cracking a virgin gas oil in a fixed-bed cracking system using the promoted bauxite and the unpromoted bauxite as catalysts.

The oil was first passed through a preheater where it was diluted with 60 lbs. of steam per barrel, then vaporized and heated to about 980° F., at which temperature, it was introduced into the reaction zone under a pressure of 85 pounds per square inch. The space velocity was controlled so that the vaporized oil contacted the catalyst at a rate of 1.25 liquid volumes of oil per volume of catalyst. The process period was 3 hours.

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The cracked hydrocarbon gases were passed from the reactor into a fractionating and separating system where the reaction products were separated from the uncracked portion. The results of the runs are compared in Table I.

Table I

	Bauxite	Bauxite+ 1.5 %SnO ₂
Temperature, °F.....	980	980
Pressure.....	85	85
Steam dilution, lbs./bbl.....	60	60
Space velocity, liq. vols./vol. of cat./hr.....	1.25	1.25
Total conversion, vol. percent of chg.....	51.2	54.7
Gasoline:		
Yield, vol. percent of chg.....	35.0	38.6
ASTM octane No. clear.....	75.6	74.4
Bromine No.....	91	93
Refractive index.....	1.427	1.422
Carbon deposition, wt. percent of chg.....	1.8	1.5
Dry gas, wt. percent of chg.....	12.9	13.6
Butanes, vol. percent of chg.....	6.2	6.1

EXAMPLE III

Another catalyst was prepared using activated alumina as a major constituent and tin oxide as a promoter as follows: A 106 gram sample of Alorca activated alumina was heated for 6 hours at 1300° F. It was then soaked for 25 minutes in 110 ml. of a solution containing 10.9 grams of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. The partially gelled mass was washed with 110 ml. of 1N NH_4OH , then drained and washed thoroughly with water by decantation. The catalyst was then heated to 1500° F. for 360 hours.

This catalyst was tested in a fixed-bed cracking system charged with a virgin gas oil identical with that used in Example I and under the same conditions of temperature and pressure. The first run was made under conditions similar to those in Example II except for a small difference in the space velocity. A second run was made at a higher space velocity for comparison with the results obtained from a run with the tin impregnated bauxite catalyst at a comparable rate.

The results from the two sets of runs are compared in the following Table II.

Table II

	SnO ₂ on Bauxite	SnO ₂ on acti- vated alumina
Temperature, °F.....	980	980
Space velocity, liq. vols./vol. of cat./hr.....	1.75	1.85
Pressure, p. s. i.....	85	85
Lbs. steam/bbl. oil.....	60	60
Total conversion, vol. per cent of chg.....	39.9	31.6
Gasoline:		
Yield, vol. per cent of chg.....	30.6	23.3
ASTM Octane No. clear.....	73.7	68.5
Bromine No.....	96	87
Carbon deposition, wt. per cent of chg.....	1.0	0.8
Dry gas, wt. per cent of chg.....	8.7	7.4
Butanes, vol. per cent of chg.....	4.2	2.3

EXAMPLE IV

In order to further illustrate the superiority of my catalyst, the following table of results is shown. These results show the comparison between my catalyst and the catalyst of tin oxide on alumina when the conversion rate is 50% in each case. These values are calculated from those in Table II. My experience has been that over this narrow range, such interpolations, or extrapolations are accurate and provide a means for obtaining comparisons at mediate or immediate conversion rates. The results are shown in Table III.

Table III

	Bauxite+ SnO ₂	Alumina+ SnO ₂
Temperature, ° F.	980	980
Space velocity, liq. vols/vol. of cat./hr.	1.41	1.02
Pressure.....	85	85
Steam dilution, lbs./bbl.	60	60
Total conversion, vol. per cent of chg.	50	50
Gasoline:		
Yield, vol. per cent of chg.	36.0	33.9
ASTM Octane No. clear.....	74.3	71.6
Bromine No.	93.3	97.4
Carbon deposition, wt. per cent of chg.	1.3	1.7
Dry Gas, wt. per cent of chg.	12.0	13.5
Butanes, vol. per cent of chg.	5.5	5.5

From the foregoing examples it is apparent that this process has many advantages. The amount of dry gas and butane formation is low. The catalytic activity is not impaired by prolonged exposure to high temperatures. The reduced rate of carbon deposition means prolonged life of the catalyst at high activity. Due to this high catalytic activity as reflected in the high conversion ratio, my catalyst permits a higher space velocity or throughput than is possible with other catalysts. This means that more high-boiling point petroleum oil may be processed in less time and with a higher yield of high octane gasoline motor fuel, less dry gas and butane formation, lower carbon deposition, and consequently, less frequent catalyst regeneration than with ordinary catalysts.

In the practicing of this invention it is obvious that variations in the arrangement may be made without invention. For instance, instead of the fixed-bed catalyst described in the examples, a fluidized bed may be used. This invention embraces such other obvious variations and modifications as come within the scope thereof. This invention is limited only by the following claims.

Having fully described my invention, I claim:

1. A method of cracking hydrocarbon oils of boiling point range higher than that of gasoline for the conversion of said oil into a high octane gasoline which comprises contacting the hydrocarbon oil in vapor form while at cracking temperature and pressure with an improved cata-

lytic mass comprising as the essential catalyst components calcined bauxite supporting 0.1% to 5% by weight of tin oxide as a promoter.

2. The invention defined in claim 1 wherein the amount of tin oxide in the catalyst is 1.5 weight per cent.

3. A process for cracking hydrocarbon oils of boiling point range higher than that of gasoline for the conversion of said petroleum oil into a high octane gasoline which comprises contacting the vaporized and preheated hydrocarbon oil at a temperature of 850° F.-1100° F. and a pressure of from 15-300 pounds per square inch with an improved catalytic mass consisting of calcined bauxite supporting 0.1 to 5 weight per cent of tin oxide as a promoter.

4. The invention defined in claim 3 wherein the amount of tin oxide in the catalyst is 1.5 weight per cent.

5. A process for cracking hydrocarbon oils of boiling point range higher than that of gasoline for the conversion of said hydrocarbon oil into a high octane gasoline which comprises contacting the vaporized and preheated petroleum oil at a temperature of about 850° F.-1100° F. and a pressure from 15-300 pounds per square inch and at a space velocity of 0.1 to 10 volumes of liquid charge per volume of catalyst per hour with an improved catalytic mass comprising as the essential catalyst components calcined bauxite supporting 0.1 to 5 weight per cent of tin oxide as a promoter.

6. The invention defined in claim 5 wherein the amount of tin oxide in the catalyst is 1.5 weight per cent.

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