April 13, 1943. W. J. MATTOX 2,316,271

TREATMENT OF HYDROCARBONS

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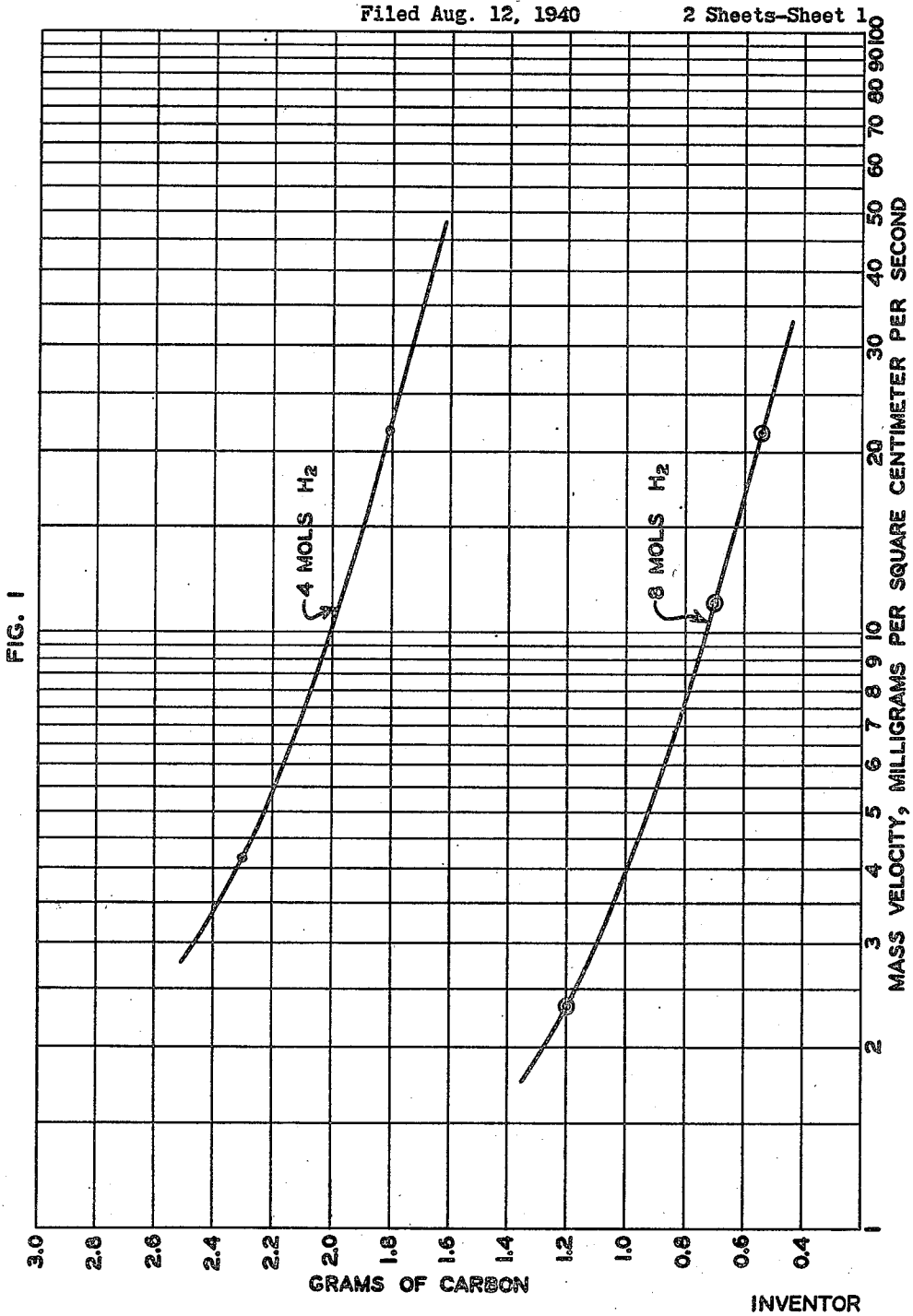


FIG. 1

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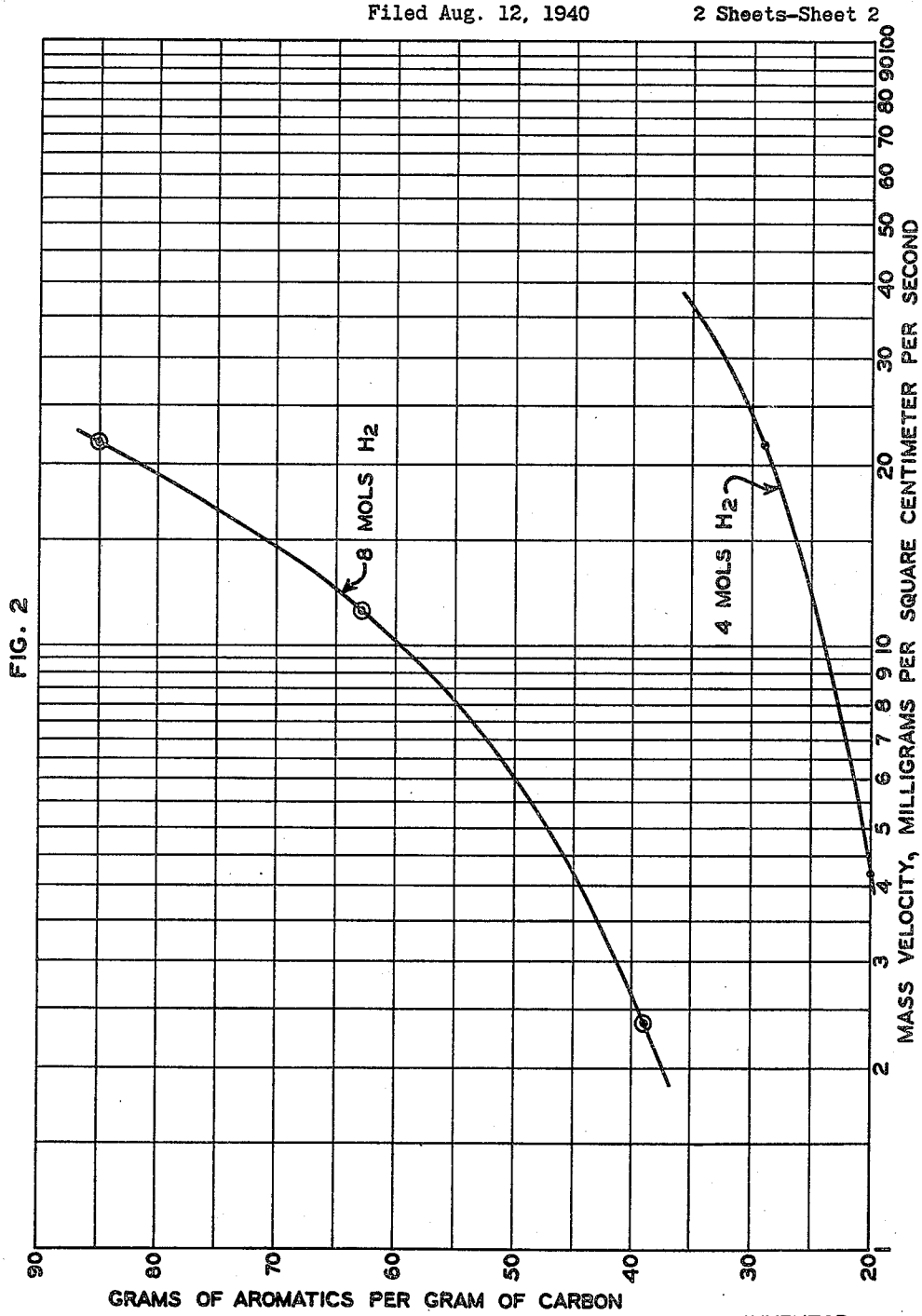


FIG. 2

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TREATMENT OF HYDROCARBONS

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8 Claims. (Cl. 260—668)

This invention relates to the treatment of aliphatic and naphthenic hydrocarbons for the dehydrogenation thereof in the presence of selected catalytic materials. It is more specifically concerned with dehydrogenation reactions of sufficient extent to cause the cycling of aliphatic hydrocarbons to produce hydrocarbons of ring structure therefrom, principally aromatic hydrocarbons.

The process is more generally applicable to individual straight chain hydrocarbons having 6 to 12 carbon atoms in straight chain arrangement since beginning with hydrocarbons having 10 carbon atoms in straight chain arrangement, there is an increasing tendency for the production of poly-nuclear rather than mono-nuclear aromatic hydrocarbons which have higher boiling points and melting points than are desired in motor fuels. However, higher molecular weight aliphatic hydrocarbons may be treated if it is desired to produce these poly-nuclear compounds in substantial yields.

The process is also applicable to the so-called "aromatization" of petroleum fractions of gasoline boiling range in which naphthenes are dehydrogenated prior to or concurrently with the dehydrogenation and cyclization of the aliphatic hydrocarbons in the mixture with them.

The art is more or less familiar at the present time with processes involving the catalytic dehydrogenation or dehydrocyclization of aliphatic hydrocarbons to produce aromatics therefrom. A wide variety of catalysts have been employed under varying conditions of operation among which may be mentioned reduced metals such as those of the iron group and more particularly nickel and a number of metal oxides subject to alternate oxidation and reduction, including oxides in the left-hand column of group VI of the periodic table comprising chromium, molybdenum, and tungsten and to a lesser extent, the corresponding oxides in group V and group IV in decreasing order of activity. While such catalysts have been found to function fairly well under accurately controlled conditions of operation depending upon the particular hydrocarbon or mixture of hydrocarbons treated, difficulties are still encountered due to the fact that there is a gradual deposition of carbon on the surfaces of catalyst particles which necessitates alternate periods of processing and reactivation during which latter periods, the carbonaceous deposits are burned off with oxidizing gases to restore the original condition of the catalyst surfaces and hence their initial activity. The present invention constitutes a marked improvement in processes of this character and comprises a process of a basic character applicable to substantially all reactions involving catalytic dehydrogenation of hydrocarbons.

In one specific embodiment the present invention comprises a process for the catalytic dehydrogenation of hydrocarbons and particularly the catalytic dehydrocyclization of aliphatic hydrocarbons by employing relatively high mass velocities above a critical value which is substantially above the mass velocities previously used in reactions of this character. The mass velocities used are preferably above 5 mg. or more of hydrocarbon per square centimeter per second. Moderate amounts of hydrogen are preferably also used in admixture with the vapors of hydrocarbons undergoing treatment.

I have determined as a result of a considerable number of experiments that the deposition of carbon on the surfaces of dehydrogenation or dehydrocyclization catalysts is markedly reduced as mass velocities ($M/A\theta$ where M=mass, A=cross-sectional area and θ time, or the mass of hydrocarbon flowing past a unit cross-sectional area per unit of time) are increased above a certain figure, while there is no decrease in the extent of the dehydrogenation or dehydrocyclization reaction. The extent of this decrease will be indicated in subsequent examples. Any mass velocity above the minimum figure stated may be employed although the upper limits will be determined to some extent by practical considerations since at higher mass velocities there are greater pressure drops through catalyst beds and if very high velocities are to be used, specially designed equipment will be necessary which presents a large catalyst surface and a lower pressure drop.

In general when employing aliphatic hydrocarbons having 6 to 12 carbon atoms in straight chain arrangement, the liquid space velocity employed may be varied from 0.1 to 20 volumes per hour per volume of catalyst, while the temperatures are varied from approximately 450 to 650° C., the pressure from atmospheric up to 1000 lbs./sq. in. (although in specific instances a pressure of from about 25 to about 100 pounds per square inch is preferred) and the ratio of the volume of added hydrogen to the volume of hydrocarbon vapors varied from 0.5 to 40, though the preferred ratio usually varies from 1 to 10. It will be obvious that by varying the particular combinations of mass velocities, space velocity, temperature, pressure, and type of

charge that a large number of operations may be conducted which are all comprised within the scope of the invention. The process is particularly applicable to the production of benzene, toluene, and xylenes, respectively from normal hexane, normal heptane, and normal octane or crude fractions of these compounds produced in the close fractionation of highly paraffinic petroleum cuts. Similarly, the corresponding 6, 7, and 8 carbon atom mono-olefins and di-olefins may be cycled or aromatized by the process with reduced carbon formation and greater overall efficiency. The only limitation upon the charging stock for the process is that the hydrocarbons charged should contain not less than 6 carbon atoms in straight chain arrangement when dehydrocyclization reactions are desired since it has not been found possible to produce cyclo-pentadiene by dehydrocyclization reactions upon normal pentane or its alkylated derivatives. Obviously when employing mono- or di-olefins instead of paraffin hydrocarbons, conditions of temperature, pressure, mass velocity, space velocity, and catalyst will require modification if best results in respect to yield and quality of products and carbon deposits are to be obtained. Similarly, if simple dehydrogenation reactions are desired without substantial dehydrocyclization, conditions of less severity will be employed.

The use as catalysts of the oxides of the elements in groups IV, V, and VI of the periodic table has already been mentioned. These oxides when used as catalysts in the present process are preferably employed on relatively inert supporting materials such as the oxides of aluminum, magnesium, or silica, or such supports as crushed firebrick, fuller's earth, clays, montmorillonite, bentonite, and in general refractory siliceous or aluminous supports. The use of chromium oxide on prepared alumina furnishes catalysts of outstanding value and similarly alumina supporting oxides of vanadium or molybdenum or cerium are particularly useful although it should be stated that none of these oxides should be considered as exactly equivalent in their dehydrogenating action on different hydrocarbons or mixtures of hydrocarbons.

In operating the process, a hydrocarbon or mixture of hydrocarbons such as a gasoline fraction is vaporized, mixed with regulated amounts of hydrogen and passed over beds of selected granular catalysts at temperatures and pressures, space velocities, and particularly mass velocities giving the optimum conversions with minimum carbon deposition. After passage over the catalyst the products are fractionated to separate products of the dehydrogenation or dehydrocyclization reactions or solvent extraction or chemical methods may be employed to remove the more reactive dehydrogenated materials and permit the recycling of the unconverted or insufficiently converted portions of the charge to further contact with the catalyst under the same or revised conditions. The passage of the mixture of hydrocarbon vapors and hydrogen over the catalyst is continued until the conversion rate drops below a practical value at which time the stream of reactants is diverted to active catalytic beds while the carbonized material is reactivated.

It is further comprised within the scope of the invention to operate reaction chambers or any type of tubular reactors in such a way that an even distribution of carbon is obtained throughout a given stationary bed. Normally in dehydrogenation or dehydrocyclization reactions, deposition of carbon increases toward the exit end of the reactor and to overcome this tendency, the temperature may be varied along the line of flow, different space velocities or mass velocities may be employed by changing the shape of the beds, different ratios of added hydrogen may be employed by injecting hydrogen along the line of flow or catalysts of varying activity may be positioned at different points in the reactor. Furthermore, operating conditions may also be controlled by recycling unused hydrogen separated in the fractionation step following the reactor, which hydrogen may contain minor amounts of other gaseous products.

The following examples are introduced to indicate the effect on carbon formation of increasing the mass velocity above values previously used in dehydrogenation and/or dehydrocyclization reactions.

Example I

A 92–207° C. boiling range Mid-Continent naphtha fraction was aromatized at 550° C., 0.5 liquid space velocity, and 50 pounds pressure with an 8% Cr_2O_3—92% Al_2O_3 catalyst and 4 moles of added hydrogen at mass velocities of 4 and 22 mg. of hydrocarbon per sq. cm. per second. The variation in carbon formation under these conditions is shown in Table 1. It will be noted that the grams of aromatics per gram of carbon formed has been increased by about 50% at the higher mass velocity.

Table 1

Hydrogen ratio, mols added per mol charge: 4
Catalyst: 8% Cr_2O_3—92% Al_2O_3, ⅛" pellets
Temperature: 550° C.
Length of processing period: 6 hours
Charge stock: 92–207° C. Mid-Continent naphtha cut
Pressure: 50 pound/sq. in.

Mass velocity, mg. naphtha/sq. cm./sec.	4.22	21.8
Liquid space vel./hr.	0.51	0.50
Yields: wt. per cent of charge:		
Total hydrocarbon	82.3	79.9
Gas, uncondensed	15.7	15.6
Gas, C_3-C_4	0.9	0.8
Carbon, per cent of charge	2.3	1.8
Aromatic yield:		
Wt. per cent of charge	47	52
Grams, aromatics formed/gm. carbon	20	29

Example II

Experiments made under the same conditions as in Example I but with 8 moles of added hydrogen are summarized in Table 2:

Table 2

Hydrogen ratio, mols added per mol charge: 8
Catalyst: 8% Cr_2O_3—92% Al_2O_3, ⅛" pellets
Temperature: 550° C.
Length of processing period: 6 hours
Charge stock: 92–207° C. Mid-Continent naphtha cut
Pressure: 50 pound/sq. in.

Mass velocity, mg. naphtha/sq. cm./sec.	2.39	11.3	21.8
Liquid space vel./hr.	0.55	0.52	0.50
Yields: wt. per cent of chg.:			
Total hydrocarbons	76.3	82.1	80.8
Gas, uncondensed	18.7	16.3	15.6
Gas, C_3-C_4	1.2	0.9	0.4
Carbon, per cent of charge	1.2	0.71	0.54
Aromatic yield:			
Wt. per cent of charge	47	45	46
Grams aromatics formed/gram of carbon	39	63	85
Composition of hydrocarbon recovery, wt. per cent:			
Paraffins	20	24	22
Olefins	18	21	21
Naphthenes	0	0	0
Aromatics	62	55	57

With 8 moles of added hydrogen at a mass velocity of 22, the carbon formation was only 0.54%

and 85 grams of aromatics was formed for each gram of carbon deposited.

The relationship of (1) mass velocity vs. carbon formation for 4 and 8 moles of added hydrogen and (2) mass velocity vs. grams of aromatics per gram of carbon are shown in the attached curves designated as Figs. 1 and 2 and drawn as a semi-logarithmic co-ordinate plot.

From Fig. 1 it is seen that the grams of carbon deposited decrease progressively with increase in mass velocity, the slope of the curves with 4 and 8 moles of hydrogen respectively being similar while the curve showing the relationship when employing 8 moles of hydrogen is much lower to indicate a lower deposition of carbon. The extrapolation of the lower curve would apparently intersect the mass velocity coordinate at some point above 100 mg./sq. cm./sec., which would theoretically correspond to zero deposition of carbon but which would undoubtedly also correspond to a prohibitive velocity on account of the accompanying high pressure drop.

The curves shown in Fig. 2 indicate the relationship between the yield of aromatics per yield of carbon and indicate that there is a striking increase in aromatic production per unit weight of carbon as a certain mass velocity is passed. The curve corresponding to the use of 8 moles of hydrogen is apparently asymptotic in character and indicates roughly that at a mass velocity of 100 mg./sq. cm./sec. carbon deposition would be negligible so that aromatics would be formed without carbon deposition. However, this lacks experimental confirmation.

I claim as my invention:

1. A process for the production of benzene from hexane which comprises passing the vapors of said hexane mixed with hydrogen in the mol. ratio of .5–40 volumes of hydrogen per volume of said hexane over a stationary bed of granular catalyst comprising essentially chromium oxide and aluminum oxide at a temperature of from about 450 to about 650° C., a pressure of from approximately 25 to approximately 100 pounds per square inch, a liquid hourly space velocity of from 0.1 to 20 volumes per volume of catalyst and at a mass velocity greater than 5 milligrams per square centimeter per second.

2. A process for the production of toluene from heptane which comprises passing the vapors of said heptane mixed with hydrogen in the mol ratio of .5–40 volumes of hydrogen per volume of said heptane over a stationary bed of granular catalyst comprising essentially chromium oxide and aluminum oxide at a temperature of from about 450 to about 650° C., a pressure of from approximately 25 to approximately 100 pounds per square inch, a liquid hourly space velocity of 0.1 to 20 volumes per volume of catalyst and at a mass velocity greater than 5 milligrams per square centimeter per second.

3. A process for the dehydrogenation of hydrocarbons having 6 to 12 carbon atoms to the molecule, which comprises combining vapors of said hydrocarbons with hydrogen and subjecting the mixture to contact with a metal oxide dehydrogenating catalyst at a temperature of from 450° to about 650° C., a liquid hourly space velocity of from 0.1 to 20 volumes per volume of catalyst, and at a mass velocity of at least 5 milligrams per square centimeter per second.

4. A process for the dehydrogenation of hydrocarbons having 6 to 12 carbon atoms in straight chain arrangement, which comprises combining vapors of said hydrocarbons with hydrogen and subjecting the mixture to contact with a metal oxide dehydrogenating catalyst at a temperature of from 450° to about 650° C., a liquid hourly space velocity of from 0.1 to 20 volumes per volume of catalyst, and at a mass velocity of at least 5 milligrams per square centimeter per second.

5. A process for the production of aromatics from hydrocarbons having 6 to 12 carbon atoms to the molecule, which comprises combining vapors of said hydrocarbons with hydrogen in the mol ratio of 0.5 to 40 volumes of hydrogen per volume of said hydrocarbons and subjecting the mixture to contact with a metal oxide dehydrogenating catalyst at a temperature of from 450° to about 650° C., a liquid hourly space velocity of from 0.1 to 20 volumes per volume of catalyst, and at a mass velocity of at least 5 milligrams per square centimeter per second.

6. A process for improving the anti-knock value of gasoline comprising hydrocarbons having 6 to 12 carbon atoms to the molecule, which comprises combining vapors of said gasoline with hydrogen and subjecting the mixture to contact with a metal oxide dehydrogenating catalyst at a temperature of from 450° to about 650° C., a liquid hourly space velocity of from 0.1 to 20 volumes per volume of catalyst, and at a mass velocity of at least 5 milligrams per square centimeter per second.

7. The process of claim 3 further characterized in that the metal oxide dehydrogenating catalyst comprises an oxide of an element appearing in the left hand column of group VI of the periodic table and selected from the class consisting of chromium, molybdenum and tungsten.

8. A process for the dehydrogenation of hydrocarbons having 6 to 12 carbon atoms to the molecule, which comprises combining vapors of said hydrocarbons with hydrogen and subjecting the mixture to contact with a molybdenum oxide dehydrogenating catalyst at a temperature of from 450° to about 650° C., a liquid hourly space velocity of from 0.1 to about 20 volumes per volume of catalyst and at a mass velocity of at least five milligrams per square centimeter per second.

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