

UNITED STATES PATENT OFFICE

2,440,673

METHOD OF UTILIZING A FUEL GAS IN
REFINING A PETROLEUM FRACTIONMinor C. K. Jones, Mountainside, N. J., assignor
to Standard Oil Development Company, a corporation of DelawareNo Drawing. Application June 15, 1946,
Serial No. 677,081

3 Claims. (Cl. 196—24)

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This invention relates to utilization of fuel gas, such as coke oven gas, water gas, or producer gas, in catalytic refining of petroleum products.

In many localities the manufacture of hydrogen has been too costly for economical use in refining petroleum products, especially where no suitable resources of natural gas are at hand.

An object of this invention is to provide a method of inexpensively utilizing available city gas or manufactured fuel gas, such as coke oven gas or water gas, containing low purity hydrogen for catalytic refining of petroleum products.

A further object is to provide a method of enriching manufactured gas, by which it is enhanced in heating value while a portion of its hydrogen content is utilized in satisfactorily refining a petroleum product.

Catalysts resistant to sulfur poisoning, such as oxides and sulfides of molybdenum and chromium, have been employed commercially in high pressure hydrogenations of low-grade petroleum fractions with requirements of fairly pure hydrogen at high pressures and in large quantities. On the other hand, the metals, such as platinum and nickel, recognized as belonging to the class of most active hydrogenation catalysts, very active at low temperatures but, in general, very sensitive to poisonous effects of sulfur compounds present in petroleum products, have not been employed commercially in refining.

In accordance with the present invention, the catalytic material employed in refining petroleum products with manufactured gas under mild conditions of pressure and temperature is very resistant to poisonous action of sulfur compounds, organic peroxides and unsaturated polymers present in petroleum products. These catalytic materials have been used in refining operations continued over 100 hours without loss of activity. They can be regenerated satisfactorily by controlled burning of carbonaceous deposits which tend to form at elevated temperatures. They function to selectively reduce the sulfur content and selectively reduce unstable diolefins in low-grade petroleum fractions. Advantageously, they function to yield an enriched fuel gas product.

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To prepare the required catalytic materials for the present purposes, a small amount of a metal or metals selected from the group consisting of platinum and palladium, e. g., 0.1 to 10% by weight, is incorporated with a carrier of the nature of alumina, which is a hydrous oxide having ultramicroscopic pores. Silica gel is another common example of this kind of carrier.

Two types of procedures used for depositing the finely-divided or colloidal metals on the carriers are: (1) impregnation of the carrier with salt solution (e. g., ammonium chloroplatinate or chloroplatinous acid), followed by slow drying, and heat decomposition of the deposited salt; and (2) mulling of the carrier in powdered form with particles of the metal (e. g., platinum black), followed by extruding or pilling. The mulled mixture is extruded wet, then dried. The pillled mixture is dry when compressed into compact form of pill or pellet. The compact form is preferred for the present method.

The pelleted catalytic material may be used in a fixed bed operation or the compact material may be granulated to smaller size for use with a fluid or moving catalyst technique.

Temperatures to be used in upgrading treatments of low-grade petroleum fractions with a fuel gas and the catalytic material are in the range from about 200° F. to 800° F. but are specifically controlled to obtain selective reduction of unstable components, such as diolefins, and desulfurization accompanied by improved antiknock values. Practical reaction zone pressure ranges from 1 to several atmospheres.

The effectiveness of the specific catalytic materials and critical requirements of conditions are indicated by the following examples and data:

Concentrated hydrogen not being available at a refinery, locally manufactured city gas (about 30% hydrogen) was used in treating a heavy naphtha product of fluid catalyst cracking for improvement in storage stability over pellets of platinized alumina containing 2% finely-divided platinum. Conditions and results are tabulated as follows:

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TABLE 1

Operating conditions:		
Temperature, ° F.	540	
Pressure, atm.	1	
Naphtha Feed Rate, v./v./hr.	1.0	
Gas Used	City Gas	
Gas Feed Rate, cu. ft./42 gal.	1500	
Catalyst Age, hrs.	40	

	Feed Gasoline	Product Gasoline	Rerun to 98% Overhead
Octane ratings:			
Motor Method, Clear	78.9	82.0	
Motor Method+3 ml. TEL/gal.	84.4	86.8	
Research Method, Clear	89.8	94.0	
Research Method+3 ml. TEL/gal.	95.4	98.0	
Gasoline inspections:			
Bromine No. cg./g.	21	17.3	
Density, at 20°/4° C.	0.829	0.830	
Lamp Sulfur, per cent.	0.075	0.082	
Phenol No.	600	200	200
Peroxide No.	23.7	Trace	Trace
ASTM Breakdown, Uninhibited	45	330	315
ASTM Breakdown+1 lb. Inhibitor/5 M gal.	75	890	795
Copper Dish Gum, Uninhibited	621	48	6
Copper Dish Gum+1 lb. Inhibitor/5 M gal.	583	36	3
Distillation:			
L. B. P., ° F.	208	212	
5%	239	239	
10%	248	250	
50%	309	311	
90%	376	378	
F. B. P.	415	419	
Recovery, per cent.	99.0	99.0	
Loss, per cent.	0.1	0.1	

¹ n-Butyl aminophenol.

The foregoing data evidence that satisfactory improvement in stability and octane rating was obtained in the treatment. For some unexplained reason, the hydrogenation refining of catalytically cracked gasoline with ordinary city gas was found to give the gasoline better octane ratings than could be obtained by refining with pure hydrogen. Outstanding is the practically complete recovery with selective reduction of diolefins and peroxides.

Further tests show that, in the treatment at 200° F. to 400° F., the peroxides are removed with less effect on the bromine number, and at 600° F. to 800° F. more desulfurization is obtained but with more saturation of the unsaturated hydrocarbon components.

Typical compositions of manufactured fuel gases, such as water gas and coke oven gas, are represented by the following:

TABLE 2

Principal fuel gas components

Fuel Gas Components	Water Gas, Per Cent	Coke Oven Gas, Per Cent
CO	32	8
CH ₄	11	27
H ₂	36	50

In using the fuel gas, hydrogen used up is compensated for by increase of the gaseous hydrocarbon component, which has a higher heating value and thus enriches the recovered gas for illuminating and combustion purposes. Certain unsaturated hydrocarbons in manufactured gas, such as indene and styrene, which are undesirable because they form gummy deposits in gas mains and meters, are also removed by this process. Furthermore, organic sulfur impurities in the gas are converted to hydrogen sulfide which can be removed easily, if desired.

The following table shows analyses of manu-

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factured gas before and after use in catalytic hydrogenation of fluid catalyst cracked naphtha. It will be seen that the main change was in the replacement of unsaturates by saturated gaseous hydrocarbons with approximately 10% increase in heat value.

TABLE 3

Catalytic purification and enrichment of manufactured gas over 2% platinum on alumina in presence of heavy catalytic naphtha

	B. t. u. per cu. ft. ¹	Percentage by Volume	
		City Gas Feed	Product Gas
Carbon Dioxide	16.4	5.2	5.3
Ethylene	2336	0.2	
Propylene	3084	0.5	
Butylene		0.6	
Oxygen		0.6	0.4
Carbon Monoxide	322	34.8	35.0
Methane	1013	7.1	9.0
Ethane	1792	6.7	7.9
Propane	2590	1.9	3.4
Butane	3370	0.8	1.2
Pentane	4016	0.8	0.8
Hydrogen	325	29.8	25.9
Nitrogen		11.0	11.1
Total		100.0	100.0
B. t. u./cu. ft.		543	591

¹ Gas volumes at 60° F. and 30" Hg dry. Data from "Fuel-Flue Gases," American Gas Association, 1940, Table No. 30, page 51.

When the catalyst is used at temperatures approaching and above 700° F., it tends to become more rapidly coked and thereupon lose activity. However, the coked catalytic material was satisfactorily regenerated by controlled burning of the coke deposit with an air-inert (nitrogen) mixture at temperatures ranging from 700° F. to 1100° F. The regenerated catalytic material was restored to original activity which is an important factor in commercial use of the precious metal catalysts.

The examples given are for the purpose of illustration and it will be understood that modifications come within the scope of the invention claimed. This invention makes economically feasible hydrogenation treatments of various organic materials and hydrocarbon stocks with low cost gas with concomitant improvement of the gas.

I claim:

1. The method of utilizing a fuel gas in refining a petroleum fraction, which comprises treating said fraction with a fuel gas containing carbon monoxide and hydrogen at 200° F. to 800° F. in the presence of a catalytic material containing a small amount of a metal from the group consisting of platinum and palladium incorporated in a hydrous oxide carrier having ultra-microscopic pores.

2. In a process of stabilizing and improving the antiknock value of a cracked petroleum naphtha, the steps which comprise passing vapor of the naphtha with a fuel gas containing carbon monoxide and hydrogen over platinized alumina containing 0.1 to 10% by weight of finely-divided platinum at 200° F. to 700° F., and reducing diolefin components of the naphtha by reaction with the hydrogen in the fuel gas.

3. The method of improving a cracked petroleum naphtha containing substantial quantities of peroxides and also containing sulfur which comprises passing said naphtha with a fuel gas containing carbon monoxide, unsaturated hydro-

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carbons and hydrogen into contact with a pel-
leted hydrous oxide carrier containing 0.1 to 10%
by weight of a metal from the class consisting of
platinum and palladium at temperatures within
the range of 200-700° F. and thereafter recover-
ing the cracked naphtha in stabilized state and the
fuel gas increased in heating value.

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