



Industry
Canada Industrie
Canada

Canada

strategis.gc.ca

Strategis Index:

CIPO  OPIC



Canadian Patents Database

12/20/2001 - 16:13:50

(11) CA 563749

(12) Patent:

(54) PROCESS FOR DEOXYGENATING AND REFORMING FISCHER-TROPSCH NAPHTHAS WITH DUAL FUNCTION CATALYSTS

(54) PROCÉDE POUR LA DESOXYGENATION ET LA REFORMATION DE NAPHTHE FISCHER-TROPSCH AVEC DES CATALYSEURS A FONCTION DOUBLE

(72)	(Country):	LEONARD N. LEUM (Not Available) PAUL M. PITTS, JR. (Not Available)
(73)	(Country):	THE ATLANTIC REFINING COMPANY
(71)	(Country):	
(74)		
(45)		Sep. 23, 1958
(22)		
(43)		
(52)		196/141 196/188
(51)		N/A

(70) International Priority (PCT) **No**

(30) Domestic priority (Canada) **None**

(76) Inventor(s) **N/A**
 (77) Assignee(s) **Unknown**

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

View or Download Images :

- Cover Page Image
- Abstract Image
- Claims Image
-

This invention relates to the catalytic conversion of Fischer-Tropsch naphthas, and more particularly to a method of catalytically deoxygenating and reforming crude Fischer-Tropsch naphthas.

5 The Fischer-Tropsch process was developed primarily for the production of motor fuels from the reaction of hydrogen and carbon monoxide at elevated temperatures and pressures in the presence of a catalyst. Many improvements have been made since the basic reaction was discovered in
10 1923. For example, improvements have been made to the original iron, cobalt, or nickel catalysts by the use of supports, promoters, superior methods of manufacture, and the like. Careful studies have been made of combinations of process conditions so that the optimum conditions are used
15 with a specific catalyst and thus instead of producing hydrocarbons ranging in molecular weight from waxy solids to those normally gaseous there is produced maximum amounts of the desired liquid products. Furthermore, technological advances in other fields have been incorporated in the
20 process - for example, the use of fluidized catalyst beds and oil-circulation techniques.

In spite of the advances made in the process, however, side reactions occur in which oxygenated compounds are produced. These side reactions are very detrimental to
25 processes designed for liquid fuel production since they

reduce the yield of the desired hydrocarbon product and likewise pose a separation problem. It has been found that in order to make the process economically feasible not only is it necessary to remove these oxygenated
5 compounds, but it is also necessary to separate the compounds so that they can be sold. These compounds consist of alcohols, aldehydes, ketones, and acids of varying degrees of complexity and consequently their separation and purification is extremely expensive.

10 For example, since most of these compounds are soluble in water they may be removed from the hydrocarbons by water washing and subsequently separated by combinations of chemical and physical methods. In some instances some of the compounds such as the alcohols may be dehydrated
15 over alumina catalysts. No effective method has been found, however, to deoxygenate the aldehydes, ketones and acids to hydrocarbons having the same number of carbon atoms as the original compound. In view of these facts it would be desirable to have a process for converting
20 the oxygen-containing compounds into useful hydrocarbon fuel components, thus obviating their removal and separation and also furnishing additional increments of the desired fuels.

The hydrocarbon portion of Fischer-Tropsch
25 naphthas is composed primarily of normal, straight chain paraffins and olefins with smaller quantities of cycloparaffins and aromatics. The actane numbers of these naphthas usually are of the order of 40, as measured by the CRFF clear method (ASTM Method D908-51). It is
30 obvious that such fuels are of little use today as motor

fuels since regular grade motor fuels on a leaded basis are over 90 in octane number and premium fuels are approaching 97 to 100.

5 It is an object of the present invention to provide a catalytic process for the conversion of the oxygenated compounds in crude Fischer-Tropsch naphthas into hydrocarbons.

10 It is a further object of this invention to catalytically reform the hydrocarbons produced from the deoxygenation of the oxygen-containing compounds of crude Fischer-Tropsch naphthas into hydrocarbons of higher octane number.

15 It is an additional object of the invention to simultaneously deoxygenate the oxygen-containing compounds of crude Fischer-Tropsch naphthas into hydrocarbons and to reform the hydrocarbons thus produced together with the hydrocarbons originally present into hydrocarbons of higher octane number.

20 Further objects will be apparent from the following detailed description of the invention.

25 It has been found in accordance with the present invention that the low octane hydrocarbon components and oxygenated compounds comprising a crude Fischer-Tropsch naphtha can be converted into high octane hydrocarbon components by contacting the naphtha with hydrogen and a dual function catalyst in combination with specific operating conditions. Although many catalysts are known to the prior art which can convert certain oxygenated compounds into hydrocarbons by dehydration, for example
30 alumina has long been known for the conversion of alcohols

to olefins, the present invention is the first catalytic process wherein a wide variety of oxygenated compounds including all of those found in crude Fischer-Tropsch naphthas not only are converted into hydrocarbons, but
5 are reformed simultaneously into hydrocarbons of high anti-knock value.

The dual function catalysts particularly applicable to the instant invention comprise an acidic metal oxide component together with a metal hydrogenation
10 component from Group VIII of the periodic system, such as iron, cobalt, nickel, platinum or palladium.

The acidic metal oxide components which have incorporated with them the Group VIII metal include: silica-alumina, silica-zirconia, silica-alumina-zirconia,
15 silica-magnesia, silica-alumina-magnesia, silica-thoria, silica-alumina-thoria, alumina-thoria, and similar oxide combinations. These metal oxide components are characterized by having exchangeable hydrogen ions in their structure. Their preparation and properties have
20 been published widely, both in patents and technical literature. Likewise, the proportions of the various individual oxides which can be combined to produce the acidic metal oxide component may vary over relatively wide ranges, as has been set forth in the same prior
25 publications. For purposes of brevity, therefore, this information will not be reiterated here in great detail.

Among the aforementioned acidic metal oxide components, silica-alumina has been found to be particularly suitable. The catalysts described in U.S.
30 patent No. 2,589,189 which comprise silica-alumina as

the acid metal oxide component and a Group VIII metal component are particularly suitable for use in the instant invention. This patent not only describes the preparation of the acidic metal oxide component, but also methods of
5 impregnating the acidic metal oxide component with the Group VIII metal.

It is to be noted that the acidic metal oxide components enumerated above all possess activity for the cracking of hydrocarbons. Silica-alumina has been widely
10 used for this purpose and consequently is readily available in a commercial form for combination with the metal hydrogenation component. Accordingly, one of the preferred catalysts of the instant invention utilizes as the acidic metal oxide component a commercial grade of
15 silica-alumina cracking catalyst containing approximately 87 per cent silica and 13 per cent alumina by weight.

It has also been found that the cracking activity of the acidic metal oxide component base need not be that of a fresh component, but that in some instances it is
20 preferred to use a component which has had its cracking activity altered by steaming, thermal treatment, or chemical deactivation. Catalysts of these types are described in U. S. patents 2,550,531 and 2,651,598. In the first of these patents, the silica-alumina component
25 was altered by treatment with steam or thermal means so that its surface area was reduced from 400-425 square meters per gram to from 10-65 square meters per gram, as determined by the adsorption of nitrogen according to the method of Brunnauer, Emmett and Teller found in the
30 Journal of the American Chemical Society, volume 60,

pages 309 et seq. (1938). In the latter patent,
No. 2,651,598, the activity of the acidic metal oxide
component was altered by the addition of an alkali metal
compound prior to incorporation of the metal hydrogenation
5 catalyst.

Instead of utilizing the surface area of the
acidic metal oxide component as the criterion of activity
of the base, it is sometimes preferable merely to measure
the reduction in catalytic cracking activity. Accordingly,
10 acidic metal oxide components may be used which have a
catalytic cracking activity in the range between 20 and 65
distillate-plus-loss, as measured according to the method
of Birkhimer, Macuga, and Leum in "A Bench Scale Test
Method for Evaluating Cracking Catalysts", Proceedings of
15 the American Petroleum Institute, Division of Refining,
Volume 27, (III) Page 90 (1947). A summary of the most
widely used methods of measuring catalytic cracking
activity including the Birkhimer et al. method appears in
"Catalytic Cracking Techniques in Review" by Marshall Sittig,
20 Petroleum Refiner, pages 274-275, Volume 31, #9, (1952).

The Birkhimer et al. reference mentioned above
gives a comparison of several methods, therefore, if it
is decided to compare the activity described in terms of
the Birkhimer et al. "D+L" with other measurements, it is
25 only necessary to refer to the comparisons mentioned in
such review.

According to the Birkhimer et al. D+L
(distillate-plus-loss) catalytic activity measurement, it
would be possible to have a theoretical maximum D+L of
30 100, however, in general for a fresh silica-alumina cracking

catalyst the maximum D+L will range between 90 and 95. Since the other catalytic activity measurements methods for measuring D+L give much lower values for a fresh silica-alumina cracking catalyst, usually of the order of 5 45-65 depending upon the particular test, it is apparent that when one specifies a D+L scale having practicable maximum activity of 90-95 the Birkhimer et al. test is being employed.

As an example, a well-known method of preparing 10 an acidic metal oxide component particularly suitable for the instant invention involves adding sulfuric acid to commercial water glass in proportions to precipitate silica hydrogel; the silica hydrogel is washed with acidulated water to remove sodium ions, after which the 15 hydrogel is dispersed in a sufficient amount of an aqueous solution of aluminum sulfate of suitable concentration so that when ammonium hydroxide is added to precipitate the alumina there is formed a silica-alumina component containing about 13 per cent by weight of alumina. The silica- 20 alumina is then washed, dried, and calcined at elevated temperatures and formed into pellets. Such a component will have a D+L from 90 to 95 in terms of the Birkhimer et al. D+L measurement set forth above. Similar methods of preparing the other components mentioned herein may be 25 used and as has been pointed out these methods are well-known to the prior art. Likewise, the proportions of the metal oxides may be varied in accordance with the prior art teachings.

Of the various Group VIII metals which may be 30 incorporated with the acidic metal oxide, iron, cobalt,

nickel, platinum, and palladium are preferred, and of these platinum is the most preferred although the other metals may be used readily inasmuch as ordinarily there are no sulfur containing compounds present in Fischer-Tropsch naphthas which would poison these metals.

Various known methods may be utilized for combining the metal hydrogenating component with the acidic metal oxide component, for example to a portion of the acidic metal oxide may be added an aqueous solution of a salt of the desired metal, such as the nitrate in the case of the iron, cobalt, or nickel, in an amount equivalent to the percentage of metal desired in the ultimate catalyst. The impregnated acidic metal oxide is then dried, calcined and thereafter reduced in a stream of hydrogen to produce the metal from the metal compound. In the event that platinum or palladium is to be utilized, the acidic metal oxide component is generally impregnated by admixing the component with an aqueous solution of chloroplatinic acid of suitable concentrations in the desired amounts. Instead of aqueous solutions of the acids aqueous solutions of the complex Werner type salts may be used, such as platinum tetramino chloride, platinum tetramino hydroxide, and similar corresponding tetravalent platinum compounds. Likewise, the corresponding complex compounds of palladium may be employed.

In using the latter type compounds the metal oxide component is heated in the aqueous solution of the complex to an elevated temperature, generally to about the boiling point of the solution, and is held at this temperature for a period of time ranging from 4 to 24 hours. After the

heating step the spent solution is drained from the metal oxide compound and the impregnated component is dried to remove excess moisture, following which step the dried impregnated metal oxide is then subjected to known
5 conventional methods for decomposing or reducing the platinum or palladium complex to produce metallic platinum or palladium on the metal oxide component. Methods for accomplishing the latter step include decomposition with air or reduction with hydrogen at elevated temperatures.

10 It has been found that amounts of the metal hydrogenating component ranging between 0.1 per cent and 10 per cent by weight of the finished catalyst give satisfactory catalysts for the process of the instant invention. Since the activity of the catalysts for de-
15 oxygenating and reforming Fischer-Tropsch naphthas depends somewhat on the particular combination of acidic metal oxide component and metal component, a considerable degree of flexibility is possible in the proportions of the two components within the broad range. Particularly good
20 results are obtained with from 3 per cent to 8 per cent by weight (based on the final catalyst) of iron, cobalt, or nickel on a silica-alumina component. If platinum or palladium is used as the metal component smaller amounts have been found to be quite effective, this being highly
25 desirable since these metals are considerably more expensive than the iron, cobalt, or nickel. In the case of platinum or palladium amounts from 0.1 per cent to 1.0 per cent by weight based on the final catalyst give extremely good results.

It is to be emphasized that the catalysts of the instant invention are not merely mixtures of two components each of which performs its expected function. The acidic metal oxide component alone will neither deoxygenate all
5 of the compounds in the naphtha, nor will it hydrogenate and reform the hydrocarbons. The hydrogenation metal alone will neither isomerize nor otherwise reform hydrocarbons. The combination of the two components, however, produces the new and highly useful process of the instant invention.

10 The reaction conditions of the process are those which have been found to be particularly suitable for reforming naphthas of petroleum origin. The conversion temperature for the reaction may range broadly between 700°F. and 1000°F., however, reaction temperatures within
15 the range of 750°F. and 950°F. are preferred. Pressures ranging between 50 and 1000 p.s.i. may be used successfully, with pressures ranging between 200 and 700 p.s.i. being preferred. The liquid hourly space velocity may range broadly from 0.5 to 6, with from 1 to 3 volumes of charge
20 per volume of catalyst per hour being preferred. From 5 to 20 mols of hydrogen per mol of charge naphtha is suitable for carrying out the reaction, with from 8 to 12 mols of hydrogen per mol of charge being preferred.

When employing the dual function catalysts
25 delineated above together with the reaction conditions set forth, the crude Fischer-Tropsch naphtha undergoes a variety of reactions. The oxygen-containing compounds are deoxygenated to produce hydrocarbons having the same number of carbon atoms as the original oxygenated compounds.
30 These hydrocarbons together with the hydrocarbons originally

present in the naphtha undergo a variety of reactions to increase their anti-knock value. For example, the normal paraffins are isomerized to produce branched chain compounds which are of higher octane value. Some of the
5 normal paraffins are dehydrocyclicized to produce aromatics and the cycloparaffins originally present are dehydrogenated to produce additional aromatics. Since aromatic hydrocarbons have extremely high octane numbers, such reactions are of particular value in raising the octane number of the
10 entire mixture. While there is generally a considerable amount of olefinic hydrocarbons present in the original naphtha and while these will be hydrogenated to paraffins of lower octane number, these paraffins likewise are isomerized so that there is no over-all loss, but generally
15 an actual increase, in anti-knock value. Finally, the heavier, higher molecular weight hydrocarbons will be hydrocracked into components of considerably higher octane value.

A highly desirable feature of the aforementioned
20 dual function catalysts is their ability to hydrocrack with the production of large fragments, rather than with the production of gas and coke. Consequently, the yields which can be obtained from this process are extremely high. It will be noted that inasmuch as the reactions which produce
25 hydrogen are in the minority as compared with the reactions which consume hydrogen, there generally will be a net over-all consumption of hydrogen in the process.

The hydrogen for the reaction may be supplied from any convenient source, provided that it is free of
30 compounds which would poison the catalyst. A convenient

source of hydrogen might be a conventional catalytic reforming process wherein petroleum naphthas are being reformed, inasmuch as such processes operate with a net production of hydrogen due to the fact that petroleum naphthas generally contain relatively large amounts of cycloparaffins which when dehydrogenated to aromatics produce the excess hydrogen. In addition to the hydrogen supplied to the process from external sources, any hydrogen remaining in the effluent product stream may be separated by conventional methods and recycled.

It should be pointed out that the hydrogen supplied to the process should not only be sufficient to satisfy the needs of the reactions enumerated, but also there should be an excess of hydrogen present in order to prevent the catalyst from becoming deactivated by the deposition of coke.

In order to demonstrate a number of important features of the instant invention, the following experiments were carried out:

EXAMPLE I

A commercial cracking catalyst comprising approximately 87 per cent of silica and 13 per cent alumina was steamed at a temperature of 1050°F. and a pressure of about 150 p.s.i. for about 5 hours to produce a component having a catalytic cracking activity of 45 D+L, as measured according to the aforementioned Birkhimer et al. method. This component was impregnated with an aqueous solution of chloroplatinic acid such that the final catalyst when dried and reduced contained 0.45 per cent by weight of platinum. Forty grams of this catalyst in the form of granules was

placed in a reactor tube fitted with external heaters in order to maintain nearly isothermal conditions throughout the catalyst bed. A Fischer-Tropsch naphtha and hydrogen were preheated and contacted with the catalyst under the conditions set forth below in Table I. The hydrocarbon portion of the Fischer-Tropsch naphtha was determined by mass spectrometer analysis and the oxygenated portion was determined by infrared analysis. Similar analyses were used to determine the composition of the effluent from the reaction. The results obtained from these operations are set forth in Table I:

TABLE I

		Run 1	Run 2		
15	Reaction Conditions				
	Temperature, °F.	850	950		
	Pressure, p.s.i.	500	500		
	Space Velocity v./v./hr.	2	2		
	H ₂ to Charge mol. ratio	10:1	10:1		
20	Analyses in Weight Percent (No Loss Basis)	Feed	Products of Run 1	Products of Run 2	
		Paraffins	38.3	85.1	64.5
		Aromatics	1.2	10.2	26.8
		Cycloparaffins and Olefins *	45.6	4.7	8.7
		Oxygenated Compounds	14.9	0	0
		Octane Number, Clear.			
		Research Method (ASTM Method (D908-51))	40.4	66.8	82.2

*Mass spectrometer analyses do not differentiate between cycloparaffins and olefins, however, from chemical analysis it is known that olefins predominate almost exclusively in this fraction of Fischer-Tropsch naphthas.

It will be noted from the above data that all of the oxygenated compounds have been converted and that the octane number of the naphtha has been materially increased. It will be noted further that it is desirable to operate
5 in the higher temperature ranges, in other words, at rather high severities in order to produce the greatest octane number increase.

The weight per cent, no loss basis, of four carbon atom and higher hydrocarbons produced was 86.1 at
10 950°F. and 89.8 at 850°F. It is apparent that the slight loss in yield when operating at the higher temperature ranges is offset by the greatly increased octane improvement.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising an acidic metal oxide component and a metal of Group VIII of the periodic system in an amount ranging from 0.1 per cent to 10 per cent by weight of the final catalyst.

2. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen at a temperature within the range of 700°F. to 1000°F., a pressure of from 500 to 1000 pounds per square inch, a liquid hourly space velocity of from 0.5 to 6 and from 5 to 20 mols. of hydrogen per mol. of charge with a catalyst comprising an acidic metal oxide component and a metal of Group VIII of the periodic system in an amount ranging from 0.1 per cent to 10 per cent by weight of the final catalyst.

3. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen at a temperature within the range of 750°F. to 950°F., a pressure of from 200 to 700 pounds per square inch, a liquid hourly space velocity of from 1 to 3 and from 8 to 12 mols. of hydrogen per mol. of charge with a catalyst

comprising an acidic metal oxide component and a metal of Group VIII of the periodic system in an amount ranging from 0.1 per cent to 10 per cent by weight of the final catalyst.

4. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising an acidic metal oxide component and from 0.1 per cent to 10 per cent by weight of the final catalyst of nickel.

5. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising an acidic metal oxide component and from 0.1 per cent to 10 per cent by weight of the final catalyst of cobalt.

6. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising an acidic metal oxide component and from 0.1 per cent to 10 per cent by weight of the final catalyst of iron.

7. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising an acidic metal oxide component and from 0.1 per cent to 1.0 per cent by weight of the final catalyst of platinum.

8. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising an acidic metal oxide component and from 0.1 per cent to 1.0 per cent by weight of the final catalyst of palladium.

9. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising a silica-alumina component and a metal of Group VIII of the periodic system in an amount ranging from 0.1 per cent to 10 per cent by weight of the final catalyst.

10. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising a silica-alumina component and from 0.1 per cent to 10 per cent by weight of the final catalyst of nickel.

11. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising silica-alumina component and from 0.1 per cent to 10 per cent by weight of the final catalyst of cobalt.

12. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under

reforming conditions with a catalyst comprising silica-alumina component and from 0.1 per cent to 10 per cent by weight of the final catalyst of iron.

13. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising a silica-alumina component and from 0.1 per cent to 1.0 per cent by weight of the final catalyst of platinum.

14. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising a silica-alumina component and from 0.1 per cent to 1.0 per cent by weight of the final catalyst of palladium.

15. A process for deoxygenating and reforming crude Fischer-Tropsch naphthas which comprises contacting the crude naphtha in the presence of hydrogen under reforming conditions with a catalyst comprising a silica-alumina component and from 0.1 per cent to 1.0 per cent by weight of the final catalyst of platinum, the silica-alumina component being characterized by having a catalytic cracking activity within a range between 20 and 65 as compared with a theoretical maximum catalytic cracking activity of 100 and a practicable maximum catalytic cracking activity of between 90 and 95 on a distillate-plus-loss scale for the measurement of the catalytic cracking activity of cracking catalysts.