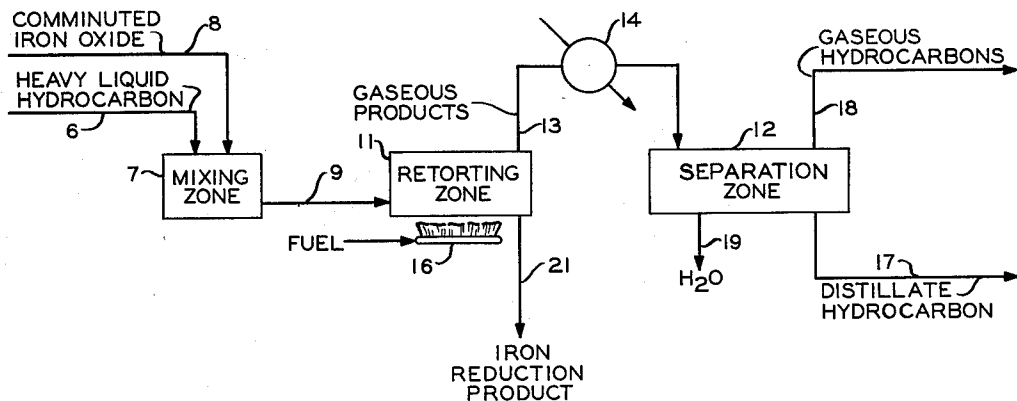


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PROCESS FOR CONCURRENT UPGRADING OF IRON
ORE AND HEAVY CRUDE OILS
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PROCESS FOR CONCURRENT UPGRADING OF IRON ORE AND HEAVY CRUDE OILS

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3 Claims. (Cl. 208—124)

This invention relates to an improved process for the beneficiation of iron ore with heavy liquid hydrocarbons. In another aspect the invention relates to a process for the concurrent upgrading of iron ore and a heavy crude oil. In still another aspect it relates to a process for the reduction of iron ore to a product in a lower oxidation state and having a considerable portion of the carbon needed for conversion to the metallic state already in place. In a yet further aspect it relates to the converting of a heavy crude oil to a product suitable for use as a distillate fuel.

Utilization of carbon, usually in the form of coke, to reduce metallic ores, principally iron ore, has long been known and practiced commercially. An alternative and technically feasible method of iron ore reduction would be to use naturally-occurring liquid hydrocarbons. However, the value of most crude oils when processed into refined products exceeds the economic benefit which might accrue from substituting a liquid hydrocarbon for inexpensive coke as an iron ore reducing agent.

There are also being found about the world in increasing quantities relatively heavy crude oils which present additional problems as to their processing into useful petroleum products in present day transportation and refining facilities.

We have discovered a process for processing these heavy crude oils, such as Monagas crude oil from Venezuela, which contain non-distillable or residual hydrocarbon components, into a hydrocarbon distillate that is suitable for use as a fuel oil by itself, or for blending with conventional fuel oil stocks. At the same time that this heavy crude oil is being commercially upgraded, an iron ore is having its oxygen content significantly decreased, and a substantial portion of the amorphous carbon needed for smelting the partially reduced ore to the metallic state has been finely dispersed throughout the ore itself.

We have further found that the gaseous products of the reaction were higher in hydrogen than would be expected from ordinary thermal decomposition of a heavy hydrocarbon liquid, which produces more methane than hydrogen. It thus appears that the presence of an iron ore had a catalytic action in the conversion of the heavy crude oil, and thereby contributed to its upgrading in a manner that would not be achieved by conventional thermal cracking alone.

It is, therefore, an object of this invention to provide a process for the beneficiation of iron ore with liquid hydrocarbons.

It is a further object of this invention to provide a process for the concurrent upgrading of iron ore and a heavy crude oil.

It is a yet further object of this invention to provide a process for the conversion of iron ore to a more readily smeltable product of a lower oxidation state and having a considerable portion of the carbon reducing agent already dispersed in the partially reduced ore.

Still another object of this invention is to provide a process for converting a heavy crude oil to a hydrocarbon product suitable for use as a distillate fuel.

Referring now to the drawing illustrating in schematic arrangement for carrying out the method of this invention, a conduit 6 is provided for supplying a heavy liquid hydrocarbon to a mixing zone 7.

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An iron ore, in finely comminuted form, is also supplied to mixing zone 7 via conveyor line 8. The liquid hydrocarbon and iron ore are intimately mixed in a weight ratio from 0.2:1 to 5:1, preferably from 0.5:1 to 2:1, in zone 7 before being passed, in slurry form, via line 9 to retorting zone 11. Retorting zone 11 is in communication with separation zone 12 via conduit 13, having a conventional cooling means 14 disposed therein. A source of controlled heat, such as oil burners 16, is provided beneath retorting zone 11. After a batch of hydrocarbon-iron ore mixture is charged to retorting zone 11, controlled heating of the zone takes place to a temperature ranging between 750 and 2000° F. The temperature chosen should be sufficient to cause chemical interaction between the components of the mixture. The chosen temperature is maintained in the retorting zone for a period of time ranging between 0.02 and 10 hours, and more preferably between 0.05 and 2 hours, in order to process a greater volume. The combination of temperature and reaction time are chosen depending upon the character of the feed mixture to be converted and can readily be determined by test. The vaporous reaction products are conducted via conduit 13, through cooling means 14, to separation zone 12 for so long as the said retorting zone continues to give off vaporous products. In separation zone 12, the liquefied distillate hydrocarbon product is separated from uncondensable gaseous hydrocarbons and water. The distillate hydrocarbon passes via conduit 17 to further blending with conventional fuel oil stocks, or may, in some cases, be suitable for use as a fuel oil by itself. The gaseous hydrocarbons and water are withdrawn from separation zone 12 via conduits 18 and 19, respectively. Concurrently, a residual solid, characterized as an iron reduction product, is withdrawn from retorting zone 11 via conduit 21. This iron reduction product has had its oxygen content significantly decreased and a substantial portion of the amorphous carbon is finely dispersed throughout the product itself, making it more suitable for further reduction to metallic iron. Thus, the iron reduction product comprises a major part of iron oxides of lower oxidation state than Fe_2O_3 , and a minor part of finely divided amorphous carbon.

The liquefied distillate hydrocarbon product of this process comprises hydrocarbons of greater than four carbon atoms having a distillation range between 170 and 800° F. It can also be further fractionated to produce distillate fuels, thermal and cracking stocks, and the like.

The heavy liquid hydrocarbons which are considered suitable for conversion in the process of this invention, are those having: less than ten percent boiling below 400° F., and preferably less than 5 percent boiling below 400° F.; a gravity not higher than 20 API; also yielding by vacuum distillation at least 30 percent of 100 penetration asphalt; and a carbon residue (Ramsbottom) that will ordinarily be greater than about 8 percent. Monagas crude oil from Venezuela is a typical heavy liquid hydrocarbon meeting the specifications, and suitable for upgrading in this invention.

The iron oxides suitable for use are those found in commercial quantities, principally iron ores. Any of a number of iron ores can be partially reduced according to this invention, but the group consisting of hematite, magnetite, taconite and minonite are particularly adapted to partial reduction here.

A better understanding of my invention and appreciation of its advantages is provided by the following example.

EXAMPLE

In these runs Monagas crude was mixed with Fe_2O_3 (Fisher certified reagent containing 99.64 percent Fe_2O_3)

in a 1/1 weight ratio. This mixture was placed in a stainless steel retort which was connected to a collecting system for both liquid and gaseous reaction products. After placing the retort in an electric furnace, the temperature was raised slowly to about 1400° F. In such operations the following semiquantitative yields of products were obtained from 96.2 grams of crude oil/ore mixture:

Iron reduction product	grams--	53.1
Unreacted Fe ₂ O ₃	do--	3.7
Distillate	do--	35.0
Water	do--	5.0
Gaseous products	cc--	300-500

Each of these fractions have been analyzed and results are presented separately.

Iron Reduction Product

The iron reduction product was a black solid essentially all of which was magnetic. This indicates that the mixture contained either Fe₃O₄ or free iron. However, other non-magnetic oxides could be present as finely dispersed solids. Coke, sulfides and carbides might also be present. X-ray diffraction shows that major compounds include Fe₃O₄ and FeO in concentrations of 50 percent each. Analysis for total carbon and sulfide sulfur allows a correction for these components. From these analyses, the composition of the iron reduction product weighing 53 grams, appears to be:

	Weight percent
Fe ₃ O ₄	40.46
FeO	40.46
FeS	0.08
Carbon	19.00
	100.00

Calculating the percent carbon from the carbon residue of the crude (11.2 percent), but neglecting the loss as CO₂, one would expect the reduction product to contain at least 10 percent carbon. The actual value of 19 percent was consistent with experimental conditions which simulate delayed coking, which procedure yields more coke than predicted by the carbon residue. It was noted that, stoichiometrically, sufficient carbon was present in the reduction product to effect complete reduction of the oxides.

Unreacted Fe₂O₃

This material, weighing 3.7 grams, was deposited on the glass wool above the furnace outlet due to foaming in early stages of the experiment. No attempt was made to analyze this fraction.

Distillate Product

Distillate began to condense in the collection system when the retort temperature reached 650-700° F. The total product, of 35 grams, represented about 80 volume percent of the crude charged. It was yellow to light brown in color. Characteristics of the distillate hydrocarbon are compared to the original crude:

	Original crude oil	Distillate HC
Carbon, wt. percent	85.2	85.2
Hydrogen, wt. percent	11.1	10.4
Sulfur, wt. percent	2.94	
API, 60/60 F	13.1	24.1
Sp. Gr., 60/60 F	0.9786	0.9094

Atmospheric distillation of the liquid fraction was also compared to the original crude:

Temperature, °F.	Original crude oil, vol. percent over	Distillate, vol. percent over
167	0.3	0.0
170		Initial Boiling Point
212	0.7	9.4
257	1.1	11.5
302	1.5	13.4
347	2.0	16.5
392	2.6	20.3
437	3.3	26.0
482	7.6	34.5
527	11.5	46.5
540		52.0

Gaseous Products

Two gas samples were submitted for mass spectrometer analysis. One of these samples was collected continuously during the reaction. The other was taken from the Dry Ice trap after the experiment was terminated. Following are the results of these analyses:

	Composite reaction gases, mol percent	Gases from trap, mol percent
Hydrogen	80.2	74.4
Carbon dioxide	1.7	3.6
Methane	10.9	12.9
Ethylene	0.7	1.5
Ethane	3.4	3.3
Propylene	1.0	0.9
Propane	1.7	2.9
Butenes		0.3
Isobutane	0.3	0.3
Total	99.9	100.1

From these analytical data it is evident that iron ore is benefited by this process which, at the same time, produces an 80 volume percent yield of upgraded crude. This may be further processed, or possibly used as a premium fuel oil. Hydrogen production is equivalent to approximately 40-60 ft.³/bbl. of crude oil processed.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention and it should be understood that the latter is not necessarily limited to the aforementioned discussion and drawing.

We claim:

1. The process of partially reducing an iron oxide and concurrently converting a heavy liquid hydrocarbon to a distillate hydrocarbon, said heavy hydrocarbon comprising less than ten percent boiling below 400° F., a gravity not higher than 20 API, and yielding by vacuum distillation at least 30 percent of 100 penetration asphalt, which comprises: intimately mixing said iron oxide in finely comminuted form with said heavy liquid hydrocarbon in a weight ratio from 1:5 to 1:0.2; charging the resulting mixture into a retorting zone; heating the said retorting zone to a temperature ranging between 750 and 2800° F. sufficient to cause chemical interaction between the components of said mixture; maintaining said temperature range for a period ranging between 0.02 and 10 hours by the end of which period said mixture substantially ceases giving off vaporous products; conducting the vaporous products to a collection zone; withdrawing the residual solid from said retorting zone as an iron reduction product comprising a major part of iron oxides of lower oxidation state than said comminuted iron oxide and a minor part of finely divided amorphous carbon; and cooling said vaporous products and condensing a liquefied distillate

hydrocarbon comprising hydrocarbons of greater than 4 carbon atoms having a distillation ranging between 170 and 800° F.

2. The process according to claim 1 wherein said iron oxide is an iron ore selected from the group consisting of hematite, magnetite, taconite, and limonite. 5

3. The process according to claim 1 wherein said liquefied distillate hydrocarbon is separated from gaseous products and water of the reaction in a zone.

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