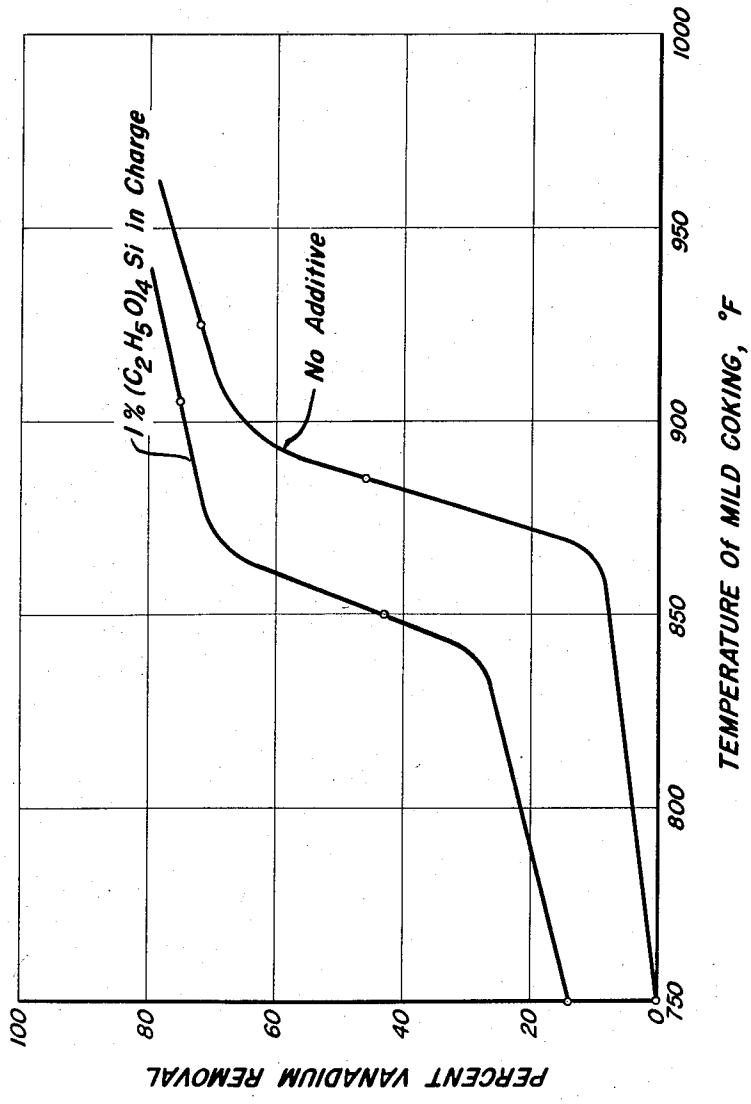
Jan. 27, 1959 L. C. GUTBERLET ET AL 2,871,185

REMOVAL OF METALS FROM REDUCED CRUDES BY MILD COKING
IN THE PRESENCE OF A SILICO ORTHO ESTER

Filed Aug. 10, 1956



INVENTORS:
Louis C. Gutberlet
Marvin J. DenHerder

BY Joseph C. Kotarski
ATTORNEY

United States Patent Office 2,871,185 Patented Jan. 27, 1959

2,871,185

REMOVAL OF METALS FROM REDUCED CRUDES BY MILD COKING IN THE PRESENCE OF A SILICO ORTHO ESTER

Louis C. Gutberlet, Cedar Lake, Ind., and Marvin J. den Herder, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application August 10, 1956, Serial No. 603,417

4 Claims. (Cl. 208—55)

This invention relates to improvements in the removal of metals from reduced crudes and in particular it concerns the removal of metals by mild coking of the reduced crude in the presence of a silico-ortho ester.

Most crude oils contain small amounts of metals such as vanadium, nickel, iron, copper, etc., which are concentrated in the highest boiling portions of the crude oil. After recovering the distillate fractions from crude oil, a reduced crude remains which has a higher concentration of metals. These ash-forming constituents interfere with further refining of the reduced crude and with the use of reduced crude as fuel. Reduced crudes are usually not catalytically cracked because their high metals content e. g. 10 to 500 p. p. m., results in poor product distribution, i. e., more coke, gas, and less gasoline, and because the catalyst becomes rapidly deactivated and must be replaced more rapidly than is required when charging gas oils. Refiners have resorted to coking of the reduced crude to produce a coke still gas oil relatively free of metals for feed to catalytic cracking, but in doing so considerable amounts of coke, gas, and low octane gasoline are formed. It would be, economically, far better to catalytically crack reduced crude if some inexpensive method of removing the metals was available.

The object of this invention is to provide a method for removing metals from reduced crude and thus improving its quality as catalytic cracking charge stock or as fuel. Another object is to provide an economic means for removing metals from reduced crudes which utilizes a mild coking operation in which coke, gas, and gasoline yields are minimized and which enables maximum production of reduced crude charging stock for catalytic cracking for the maximum production of high octane gasoline. A further object of this invention is to provide an improved mild coking process for reduced crude which uses lower temperatures and/or higher space velocities and thus reduces equipment and processing costs. Other objects and advantages of the invention will be apparent from the detailed description thereof.

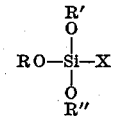
According to the invention, the metals content of reduced crudes is reduced by mildly coking a mixture of the reduced crude and between about 0.01 to 5 percent, preferably about 0.1 to 1 percent, based on reduced crude of a silico-ortho ester such as tetraethyl orthosilicate, dimethyl diethyl orthosilicate, ethyl methane orthosiliconate, or the like. The mild coking is carried out under conditions so that a portion of the reduced crude is in the liquid state during the coking operation. The amount of coke formed is limited to not more than the amount of carbon residue contained in the reduced crude as measured by the Ramsbottom carbon content of the reduced crude charged. These mild coking conditions comprise a temperature between about 750° and 900° F., and a space velocity of between about 5 and 500 liquid volumes of charged reduced crude per hour per volume of coking zone, the higher space velocities being used when the higher temperatures are employed. To our surprise it has been found that by carrying out the mild

coking in the presence of the silico-ortho esters, lower temperatures and/or higher space velocities can be used while still obtaining at least the same amount of demetallization. This enables a reduction in the operating costs and/or investment costs of the mild coking step. The mild coking can be carried out by using soaking drums which may contain a contact material such as clay, coke, etc., if desired, delayed coking equipment, in the furnace tubes of heaters, transfer lines, etc. Any free coke can then be removed by conventional means such as settling and/or filtration, etc. from the demetallized reduced crude and the latter is then suitable for use as fuel or catalytic cracking charge stock. By this method maximum removal of metals, nitrogen and sulfur is obtained with the minimum formation of coke, gas and low octane gasoline during the mild coking step.

Reduced crudes in general may be used as charge stocks in this invention. Reduced crudes may be obtained by atmospheric or vacuum distillation of crude oil to produce 5 to 75% reduced crude. They usually have initial boiling points which may range between 400 and 900° F. The metals content of reduced crudes usually varies between about 5 and 500 p. p. m. or even higher. Preferred feed stocks for catalytic cracking have a metals content of less than 1–5 p. p. m.

The silico-ortho esters are employed in an amount between about 0.01 and 5%, preferably 0.1 to 1% by volume based upon the reduced crude charged. Tetraethyl ortho-silicate is very effective in the practice of this invention. Various other silico-ortho esters which may be used are those such as: methyl orthosilicate, methyl orthosilicoformate, methyl orthochlorosilicoformate, methyl ethane orthosiliconate, trimethyl ethyl orthosilicate, hexamethyoxysiloxane, triethyl methyl orthosilicate, triethoxysilicon acetate, ethyl diethoxysilicon acetate, ethyl ethane orthosiliconate, ethyl butane orthosiliconate, triethyl amyl orthosilicate.

The general formula of some of the preferred silico-ortho esters, which preferably have less than 20 carbon atoms per molecule, is as follows:



where R, R′ and R″ are hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl, etc. and X is hydrogen, a hydrocarbon such as R, an alkoxyl or phenoxyl or carboxyl radical, or a halogen or sulfur atom. The hydrocarbon radicals may be substituted with other functional groups, such as halogen, sulfur, carboxyl groups, etc.

The mild coking of the reduced crude in the presence of the silico-ortho ester is carried out under conditions wherein a portion of the reduced crude remains a liquid during the mild coking step. By the term "mild coking" it is meant coking the reduced crude to such an extent that the amount of coke formed is not more than the carbon residue of the reduced crude as measured by its Ramsbottom carbon content. This latter measurement is a measure of the amount of carbonaceous residue which would be formed by distilling a reduced crude and it provides an indication of its coke forming propensity. The residue formed during evaporation is not entirely carbon but is a coke. ASTM D524–52T describes the test for Ramsbottom coke. The amount of coke formed in the mild coking step is usually less than the Ramsbottom carbon content. After mild coking, it is usually noted that the sum of the coke formed, plus the Ramsbottom carbon content of the mildly coked and demetallized reduced crude, is equal to the Ramsbottom carbon

content of the reduced crude charged to the mild coking operation. The amount of coke formed is frequently between about 1 and 5% of the reduced crude, depending upon the particular quality of the crude and the extent to which it is reduced. The greater the extent of reduction, the greater is the concentration of the carbon residue in the reduced crude and consequently greater amounts of coke are formed during the mild coking operations wherein the metals are removed.

It has been found that when reduced crude containing undesirable amounts of metals is heated to the temperature at which incipient coking occurs, the metals content of the reduced crude begins to decrease. As the temperature of the mild coking is further increased, by a small incremental increase of 10° F. or so, it has been noted that the removal of metals increases at a very rapid rate. Over a temperature range of about 40 to 50° F. above the temperature at which incipient coking begins, there is a precipitous increase in metals removal. Similarly, there is a precipitous increase in the amount of coke formed, a precipitous decrease in the amount of nitrogen and sulfur compounds remaining in the oil and a precipitous decrease in the Ramsbottom carbon content of the reduced crude. Within this narrow temperature range, a small amount of gas and gasoline boiling range hydrocarbons are produced. It has further been noted that as the coking temperature is increased above this range of 40 to 50° F. higher than the incipient coking temperature, there is essentially no further removal of metals within the coke formed, i. e., the metals removal remains approximately constant, usually at about 80 to 95% metals removal. However, coking occurs at an increased rate along with the accelerated formation of gas and gasoline. If the temperature is maintained between 40–50° F. higher than the incipient coking, substantially all of the metals which can possibly be removed will be removed in the coke formed and the amount of gas and gasoline would be minimized. For example, a 52% reduced crude can be mildly coked at about 800° F. at an LHSV of 40–50 with the formation of about 2.5% coke and 20 s. c. f./bbl. of gas and 2.5% gasoline; whereas at 850° F. approximately 3.5% coke, 125 s. c. f./bbl. of gas and 5% of gasoline will be formed. The gas is only useful as fuel and the gasoline formed has the much lower octane number of coker gasoline rather than the high octane gasoline which would be formed if the equivalent amount of reduced crude was instead catalytically cracked to gasoline.

The mild coking is carried out at a temperature between about 750 and 900° F. A space velocity of between about 5 and 500 liquid volumes of charged reduced crude per hour per volume of coking zone is employed. Pressures ranging from subatmospheric to 500 p. s. i. or higher may be used during the coking operation. When the higher temperatures, within the range specified, are used, the higher space velocities are also employed; and conversely, lower space velocities are used when lower temperatures are employed. For example, approximately the same extent of demetallizing can be obtained by the mild coking of a 50% reduced crude at atmospheric pressure under the following conditions of temperature and space velocity; 850° F. and 320 LHSV, 800° F. and 100 LHSV, 775° F. and 20 LHSV. When the higher boiling reduced crudes, i. e., the more fully reduced crudes are charged to the mild coking operation, a higher temperature and lower space velocity must generally be employed. The greater the extent of reduction of the crude, the higher the temperature and/or the lower the space velocity which is used. Generally lower temperatures and/or higher space velocities are employed with the lower operating pressures. Conversely, higher temperatures and/or lower space velocities are used with the higher operating pressures.

Any suitable equipment may be used in carrying out the mild coking step. For example, the reduced crude and silico-ortho ester can be passed either upflow or downflow through soaking drums under the proper conditions of temperature and space velocity. The soaking drums may contain a contact material such as clay, coke, pumice, bauxite or the like, upon which coke may be laid down. The mild coking may be carried out in modified delayed coking equipment or in coking equipment in which steam is introduced to reduce hydrocarbon partial pressure. It may be carried out in furnace tubes or in transfer lines under appropriate conditions of temperature and space velocity. Any free coke in which the metals are deposited can then be removed from the liquid by conventional means, such as settling, and/or filtration, the use of hydrocyclones, etc. The demetallized reduced crude can then be used as fuel or catalytic cracking charge stock. When proper catalytic cracking charge stocks for fluid cracking are utilized, it may not, in all instances, be necessary to remove the coke from the reduced crude before sending it to catalytic cracking. During the fluidized catalytic cracking operation, the coke is eventually transferred to the regenerator along with deactivated catalyst and during regeneration the coke will be burned and the metal fines removed and discarded from the regenerator, thus avoiding contamination of the active cracking catalyst and also eliminating a coke filtration or settling step.

A number of experiments were carried out which illustrate the fact that when a metals-containing reduced crude is mildly coked in the presence of the silico-ortho ester, a greater amount of metals is removed than occurs when the reduced crude is mildly coked in the absence of the silico-ortho ester. These experiments were carried out by passing a 52% reduced crude containing varied amounts of tetraethyl ortho-silicate downflow through a one-inch I. D. electrically heated pipe reactor about 30 inches long. The pipe was packed with 6–14 mesh pumice. Experiments were carried out in the presence of a hydrogen atmosphere and also in the presence of a nitrogen atmosphere. The mild coking was carried out at 850° F., at a space velocity of 5 volumes of reduced crude charged/hour/volume of pumic in the reactor, and at a pressure of 50 p. s. i. g., nitrogen or hydrogen being introduced into the feed in the amount of 3000 s. c. f./bbl. The product was removed from the bottom of the reactor and passed to a separator to remove gases at atmospheric pressure. The liquid was then analyzed for its metals content by mass spectrograph. Liquid yields in the neighborhood of 100% were obtained with coke yields of about 3%, based upon reduced crude. The results obtained in the experiments are shown in Table I which follows:

Table I

Volume percent $(C_2H_5O)_4Si$	Hydrogen atmosphere (p. p. m.)			Nitrogen atmosphere (p. p. m.)		
	Fe	Ni	V	Fe	Ni	V
0	1.3	3.2	6.0	1.1	2.0	6.0
0.1	1.5	2.1	3.4	0.6	0.4	1.2
1.0	1.1	0.9	1.3	0.6	1.0	1.3
Reduced crude charged	7.1	7.8	20			

It is evident that either in a hydrogen atmosphere or a nitrogen atmosphere, the presence of the silico-ortho ester increases the extent of metals removal which is obtained during the mild coking operation. Somewhat less coke was formed in the experiments carried out in the hydrogen atmosphere and a slightly poorer degree of demetallization than occurred in the nitrogen atmosphere was obtained. The experiments carried out in the nitrogen atmosphere simulate the conditions and results which would be obtained in actual operation. The results show that when no silico-ortho ester was added, the extent of demetallization was about 74%; whereas when 0.1%

tetraethyl ortho-silicate was used, the extent of demetallization was 94%.

An additional series of experiments was carried out which show that by mild coking of the reduced crude in the presence of the silico-ortho ester, lower temperatures may be employed in obtaining the same extent of metals reduction. In these experiments, samples of the same 52% reduced crude were passed at atmospheric pressure, with and without 1.0 volume percent of ethyl ortho-silicate, at temperatures varied between 750° F. and 1000° F. at a space velocity of about 320 liquid volumes of reduced crude charged/hour/volume of free space in the reactor, upflow through an electrially heated 40 cm. unpacked stainless steel tube of one-quarter-inch I. D. The lower 30 cm. of the reactor tube functioned as a preheater section and the upper 10 cm. zone functioned as the mild coking reactor. The product was collected, the gas separated therefrom, and the liquid product was analyzed for vanadium content by mass spectograph. The results which were obtained in these experiments are shown in Table II which follows:

Table II

Temp., ° F. of mild coking	Volume percent $(C_2H_5O)_4Si$	Percentage of vanadium removed
750	0	0
885	0	46
925	0	72
750	1.0	14
850	1.0	43
905	1.0	75

It will be noted from the above data, and even more clearly from the attached figure, which is a graphical presentation of the data obtained, that by carrying out the mild coking of the reduced crude in the presence of the silico-ortho ester the mild coking temperature can be reduced by approximately 50° F., i. e., from 900° F. down to 850° F. while still obtaining the same extent of metals removal.

While the invention has been described with reference to certain specific examples, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as would occur to one skilled in this art.

What is claimed is:

1. The method of reducing the metals content of reduced crudes which comprise mildly coking an intimate mixture of the reduced crude and between about 0.01 to 5 percent by volume based on reduced crude of a silico-ortho ester, said mild coking being carried out under conditions wherein a portion of the reduced crude is liquid and wherein the amount of coke formed is not more than the Ramsbottom carbon content of the reduced crude charged, the mild coking conditions comprising a temperature between about 750° and 900° F. and a space velocity of between about 5 and 500 liquid volumes of charged reduced crude per hour per volume of coking zone, the higher space velocities being employed with the higher temperatures.

2. The method of claim 1 wherein tetraethyl ortho-silicate is employed in an amount between about 0.1 and 1 percent by volume based upon reduced crude charged.

3. The method of claim 1 wherein the mildly coked reduced crude is separated from the coke formed and then cracked in the presence of a silica base cracking catalyst.

4. The method of claim 1 wherein the coking zone contains a contact material.

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