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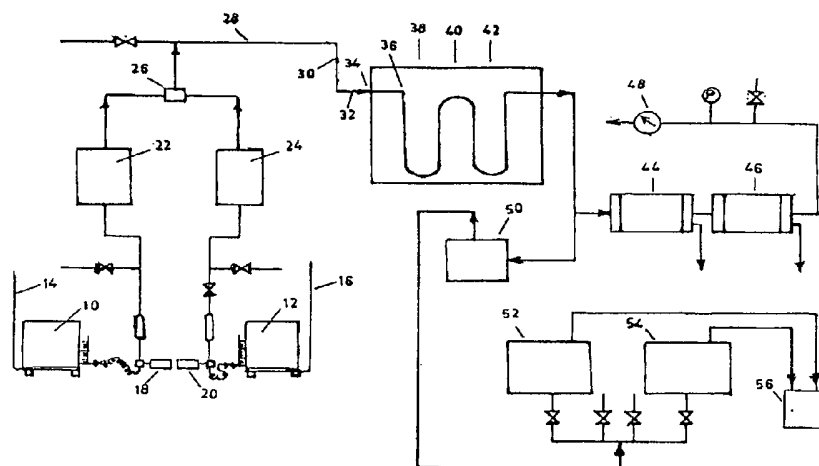
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(54) Title: PROCESS FOR THERMAL CRACKING HYDROCARBONS



(57) Abstract: A process for thermal cracking of hydrocarbons in a pyrolysis furnace is disclosed. The improvement comprises inhibiting coke formation on the surface and/or coils of said pyrolysis furnace by adding to the hydrocarbon feed stock, from 100-300 ppmw of sulfur oil which is a mixture of organic disulfides in the carbon number range of C₂-C₄, and subjecting said feed to cracking at a temperature in the range of 820-855 °C.

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PROCESS FOR THERMAL CRACKING HYDROCARBONS

Field of the invention

The present invention relates to the process for the thermal cracking of hydrocarbons. More particularly, the present invention relates to a method of inhibiting coke formation on surface of the cracking coils. It also relates to anti coking additives that are useful in inhibiting coke formation on such cracking coil surfaces and related equipment.

Background of the invention

Thermal cracking of hydrocarbon feedstocks in presence of steam is the most important commercial process for the production of light olefins like ethylene, propylene, butanes and butadienes and aromatics, the main feedstocks of the petrochemical industry. The hydrocarbon feed stocks range from ethane to vacuum gas oils and any combination thereof.

The operation is generally carried out in gas fired furnaces containing long vertical coils or tubes in parallel. The number of coils in the furnace is a function of the ethylene capacity per furnace. The hydrocarbon is diluted with steam to minimize undesired side reactions and is preheated up to the required transition temperature for pyrolysis in the radiation section. This temperature is known as cross over temperature. The cross over temperature is in the range of 600-650 °C. The steam to hydrocarbon ratio by weight is from 0.3 to 0.5 depending on the feedstock. Cracking takes place in radiation section. In radiation section high heat fluxes can be achieved. The process gas temperature at the coil outlet is around 820-840 °C. The coil inlet pressure is in the range of 1.5 to 2 kg/ cm²g. The residence time is in the range of 0.4 to 0.66 s. The effluent from the furnace is rapidly quenched by transfer line exchanger (TLE) in which high pressure steam is produced. The rapid quench reduces loss of olefins by minimizing secondary reactions. The effluent from TLE is fractionated into its constituents or groups of them.

Thermal cracking of hydrocarbon liquids and gases is always accompanied by formation of coke. The coke is deposited on the coil surface and metal surfaces of the processing equipment. The coke on coil surface hampers the heat transfer from the furnace to the reacting gas. To compensate for this, the external tube skin temperature has to be increased without exceeding the limits imposed by metallurgy. The reduction in coil

diameter due to the coke layer increases the coil pressure drop. This in turn leads to higher coil inlet pressure, which is detrimental to the ethylene yield. Another detrimental effect is, coking may lead to carbonization. Hence, the coke has to be removed periodically by taking the furnace offline and burning the coke in presence of steam and air. Decoking
5 takes one to two days time and is done generally once in 30-120 days depending on the severity and feed type. Decoking results in increased downtime and it is also relatively expensive and requires labour and energy. Hence attempts to improve the economics in all aspects like finding a new additive or cheap alternate is always welcome.

Various approaches have been reported to inhibit coke formation in thermal
10 cracking of hydrocarbons. Sulfur compounds, mostly dimethyl disulfide (DMDS) are introduced into hydrocarbon feed to reduce coke formation. Some of the components of the coil material like nickel catalyses the reaction of hydrocarbons with steam and catalyses their decomposition to coke. Sulfur decreases the catalytic activity of the nickel by acting as a catalyst poison. The sulfur compounds are removed from the effluent
15 process gas by contracting with an aqueous caustic solution in scrubber. The use of sulfur compounds to control coke formation in thermal cracking of hydrocarbons is shown in the prior art.

Description of prior art

According to GB Patent No. 1,077,918, GB Patent No. 1,090,983, German Patent
20 No. 1,234,205, French Patent No. 1,468,873 and French Patent 1,497,055, sulfur reduces coke and carbon monoxide formation in ethylene furnaces. U.S. Patent No. 4,116,812 describes a process of inhibiting coke formation at temperatures from 260 to 815 °C by adding organo-sulfur compounds. U.S. Patent No. 5,463,159 describes a method of treating ethylene furnaces with hydrogen sulfide to reduce coke and/or coke formation.
25 U.S. Patents No. 5,565,087 and 5,616,236 disclose method sfor inhibiting coke and carbon monoxide formation by treating the cracker tubes with sulfur compounds in the presence of hydrogen U.S. Patent No. 5,954,943 discloses a method of reducing coke deposition in cracking furnaces with a combination of sulfur and phosphorus containing compounds. To summarize, optimum amount of sulfur in the form of mostly DMDS is
30 used in commercial crackers to reduce coke and carbon monoxide formation. Various other anti coking additives to reduce coke formation have been patented. U.S. Patent No.

4,666,583 discloses a method of reducing coke on coil by contacting the metal with an additive selected from the group of gallium and tin and a metal with an additive selected from the group of gallium and tin and a combination of gallium and antimony. U.S. Patent No. 4,962,264 discloses a method of reducing coke by adding rare earth elements or compounds such as cerium and lanthanum elements or compounds to the hydrocarbon feed. U.S. Patent No. 5,000,836 discloses that coke can be inhibited by adding a combination of molybdenum and boron to hydrocarbon feed. U.S. Patent No. 5,128,023 discloses that a combination of boron compound and a dihydroxybenzene added to hydrocarbon feed reduces coke formation and deposition. U.S. Patent No. 5,358,626 discloses a method of controlling coke by adding a mixture of Group 1 A metal salt, a Group IIA metal salt and a boron acid or salt thereof to the hydrocarbon feed stock. Various phosphorous based additives such as phosphoric acid (U.S. Patent No. 3,531,394), phosphate and phosphite mono and diesters (U.S. Patent No. 4,105,540), amine complexes of phosphate, phosphite, thiophosphate and thiophosphite mono and diesters (U.S. Patent Nos. 4,542,253 and 4,842,716), triphenyl phosphine (U.S. Patent No. 4,835,332), triphenyl phosphine oxide (U.S. Patent No. 4,900,426), phosphorothioate (U.S. Patent No. 5,354,450) were reported to inhibit coke formation coke comparable to element based additives.

All these above methods involve synthesis of the additive which are mostly very expensive and proper care should be taken for commercial trials so that they are not detrimental to downstream processes. It was found that some of the phosphorus based additives caused convection section corrosion problems and adversely effected catalyst performance in down stream operations. Hence, there is constant need for the development of a readily available and cost effective additive in reducing coke deposition.

Objects of the inventon

Accordingly, it is an object of the present invention to provide a process for the thermal cracking of hydrocarbons which avoids the drawbacks of the prior art.

It is another object of the present invention to provide a method of inhibiting coke formation on surface of the cracking coils.

It is yet another object of the present invention to provide anti coking additives that are useful in inhibiting coke formation on such cracking coil surfaces and related equipment

It is still another object of the present invention to test sulfur oil, a mixture of organic disulfides of C₂-C₄ carbon number range, which is a low value product from petroleum refinery, in coke inhibition

It is yet another object of the present invention to provide a cheap alternate for costly commercial additives.

It is also the objective of the invention of provide a procedure to measure coke profile using as specially designed 'w' coil (SDCCPM).

It is further the objective of the invention to develop a method to test anti coking additives.

Summary of the invention

The above and other objects of the present invention are achieved by the process of the present invention. According the present invention provides a method for inhibiting coke formation and deposition of coke on metal surfaces of a pyrolysis furnace which is used for thermal cracking of hydrocarbons. The method comprises of adding a 100-300 ppmw amount of sulfur oil which is a mixture of organic disulfides in the carbon number range of C₂-C₄, to the hydrocarbon feed and subjecting the feed to cracking temperatures in the range of 820-855 °C.

In a preferred feature, the additive is a low value product from petroleum refinery finding useful application in coke inhibition.

In another feature, organic disulfides comprise alkyl disulfides, wherein the preferred alkyl radicals are methyl and ethyl and the typical sulfur content in sulfur oil is 60%

In the present invention, the additive is as effective as commercial sulfur additives and the sulfur concentration in the feed is most preferably between 140 and 150 ppmw.

The sulfur content in gas and liquid products is within allowable limits.

In a preferred embodiment, the additive is decomposable at reaction conditions and completely converted in the furnace.

In another preferred embodiment, the metal surface is a cracker coil wall, said metal being iron or nickel or both.

Preferably, the feed is any hydrocarbon or their mixtures that can be cracked for olefins production.

5 Preferably, the coil is specially designed for coke profile measurement without breaking the coil

Detailed description

The present invention relates to a process for thermal cracking of hydrocarbons. More particularly, the present invention relates to a method of inhibiting coke formation on surface of the cracking coils. It also relates to anti coking additives that are useful in
10 inhibiting coke formation on such cracking coil surfaces and related equipment.

Thus, according to the present invention, there is provided a process for thermal cracking of hydrocarbons which comprises feeding said hydrocarbon feed to a pyrolysis furnace, and subjecting it to hydrocracking characterized in that from 100-300 ppmw of sulfur oil which is a mixture of organic disulfides in the carbon number range of C₂-C₄, is
15 added to said hydrocarbon feed and said feed is subjected to cracking at a temperature in the range of 820-855 °C.

The present invention also relates to a method for inhibiting coke formation on the surface and/or coils of a pyrolysis furnace during a hydrocracking process, which
20 comprises adding to the hydrocarbon feed stock, from 100-300 ppmw of sulfur oil which is a mixture of organic disulfides in the carbon number range of C₂-C₄, and subjecting said feed to cracking at a temperature in the range of 820-855 °C.

The process of the present invention and the additive employed in the process are described in greater detail herein.

25 Source of sulfur oil

Sulfur oil is produced from LPG Mercaptan oxidation (merox) units of refining complex as a byproduct when mercaptan laden LPG is treated with sodium hydroxide for mercaptans removal. Care is taken to have consistent quality of sulfur oil. Sodium is highly detrimental to any process, heaters/ furnaces as it promotes coking leading to
30 shorter life between two decokings. Caustic carryover into the sulfur oil is minimized within accepted tolerance limits. The mercaptans in LPG is restricted to lower molecular

weight only due to controlled boiling range of LPG. This results in an indirect control on boiling range of sulfur oil. Trace metals in the merox unit product streams are monitored to maintain the quality.

Typical properties of sulfur oil

5 The sulfur oil used in the process of the present invention will typically have the following characteristics:

	S, Wt%	:	60.0 typical
	Critical temperature, C	:	351
	Critical pressure, bars	:	47.8
10	Boiling range, °C	:	110-180
	Density (20) g/cc	:	1.03
	Viscosity (20), cps	:	0.597
	Vapor pressure (20), mbar	:	13.6
	Surface tension (20), dynes/cm	:	33.6
15	Specific heat (25), KJ/Kg-K	:	1.521
	Na, ppmw	:	1.0 max
	Co, ppmw	:	0.25 max
	Cu, ppmw	:	0.10 max
	Fe, ppmw	:	0.20 max

20

The present invention will now be described in greater detail with reference to the accompanying drawings and Examples which are merely for the purposes of illustration and should not be construed to constitute a limitation on the scope of the invention..

Referring to the accompanying drawings:

- 25 FIG. 1 is a schematic representation of the naphtha cracker pilot plant;
 FIG. 2 is a typical temperature profile;
 FIG. 3 is coke profile of the coil in the hydocracking furnace;
 FIG. 4 is comparison of coke profiles of blank runs with additives;
 FIG. 5 is relative reduction of coke rate with respect to blank run;
 30 FIG. 6 is spalling rate of bland run and runs with additives;

In tubular reactors coke is not deposited uniformly even under isothermal operation, but rather according to a profile. For any developmental activity like testing of anti coking additives, information on the coke profile is essential. Unless the reactor is cut into pieces, there is no other way of determining the coke profile in a tubular reactor. Hence, a reactor has been designed specifically for this purpose with a provision to measure coke profile. Figure 1 represents the schematic representation of the naphtha cracker pilot plant with a coil, the design of which is very novel in which the present invention has been carried out.

Naphtha and water are stored in two SS tanks, 10, 12 at atmospheric pressure. The tanks are provided with level gauges using which the flow rate of the feeds can be checked regularly. The tanks are placed on electronic weighing balances 14, 16 of 50 kg. capacity each. The amount of feed consumed in the particular run is given by these balances. There are two metering pumps 18, 20 of 20 l/h capacity each for the pumping of the feeds. The suction is taken from the storage tanks through spiral tube to minimize pulsations in the feed flow.

There are two vaporizers, naphtha vaporizer 22 and water vaporizer 24 made of SS316. The heat is supplied by electrically heated furnaces to vaporize the naphtha and water. During a typical run the outlets of vaporizers are sent to a mixer 26 where the temperature is raised to around 200 to 250 °C. The mixer outlet flows through three electrically heated super heaters 28, 30,32 and enters the top of the furnace reactor tube inlet 34 at 600 °C which is taken as cross over temperature.

The coil 36 is 'w type' with a provision to measure temperature and coke profiles. The coke samplers (3.4x1.2 cm) made of same material as the coil can be inserted at the top and bottom location of each pass of the coil. The reactor tube is 5.30m long, made of Incoloy 800H, and has an internal diameter of 26.7 mm. Thermowells of 0.73 m long and 17 mm diameter, made of same material as the coil fixed from the top in each pass of the coil, serves as a concentric insert. This insert provides turbulent flow within the reactor. The coil is suspended in an electrically heated furnace with three zones 38, 40 and 42. The furnace is 1.856m long and 0.5842m wide and 1.174 m high. Each zone temperature can be independently controlled to set to any desired temperature profile in the coil. Sixteen thermocouples are located in the reactor coil to measure process gas temperature

profile. The external wall temperature is measured at 12 locations. Thermocouples are located in the air space between the heating element and tube, along the outer surface of the coil and in the process flow stream. The furnace exit gases are quenched to around 600 °C. The naphtha feed flow rate can be varied up to 10 kg/h. The gases are further cooled in two heat changers 44, 46 in series to condense the stream and heavier fractions in the gas mixture. The condensed water and liquid are then collected and weighed for mass balance calculations. Non condensed gases were further cooled and measured by a wet gas meter 48. A small portion of furnace outlet stream is passed through Fluid Data. Sample conditioner 50 and the gas from the top of the conditioner is sent for online analysis by two GCs 52, 54. The output of the GCs is sent to PC 56 for area intergration and processing. The pilot plant is connected with DARWIN system, which controls the process parameters and has several on-line functions like data acquisition and data treatment.

The cracked gas samples is simultaneously analysed on two gas chromatographic (GC) systems. Hydrogen and methane are detected by a thermal conductivity detector (TCD) in the first system (HP 3362). The analysis takes about 5 minutes. All the hydrocarbons except hydrogen are detected by a flame ionization detector on second system (HP 5890) and this analysis takes around 60 minutes. Peak identification and integration is performed by a commercial integration packages. With these, the product distribution in terms of weight percentage can be determined. Since the feed flow rate is known, yields of products % wt/wt of HC feed and material balance can be calculated.

Test procedure

For a typical run the furnace is turned on and the temperature is slowly increased while air is fed in continuously. After desired temperature profile is established, water is introduced in to the unit. After few minutes, air is discontinued and naphtha is fed into the unit. The flow rates of naphtha and water are set in such a way that the desire dilution ratio is maintained. The temperature of the furnace is dropped, as soon as naphtha is introduced into the reactor due to the endothermic reactions. The temperature is increased slowly to reach to the desired temperature profile and coil outlet temperature in 20 to 30 minutes. The product gases are analysed by using two gas chromatographs. Typical

material balance is performed for an hour period by taking the weights of naphtha and water, the amount of liquid product collected, total amount of gas measured through gas flow meter during the one hour period and product gas analysed. During a typical 12h coking, run the product gas is analysed once in four hours. After completion of a run, the reactor is cooled and coke samplers are weighed to obtain surface coke. The spalled coke collected in the dead leg is measured. The reactor is then steam-air decoked.

Results

Coke profile

The knowledge of coke profile and coking rate of a coil is essential for evaluating various anti coking additives. Series of accelerated coking experiment have been carried out in this unit to obtain coke profile in the coil during thermal cracking of naphtha. The amount of coke deposited is calculated from the weight gain of the coke samplers after run for 12 hours. The coke samplers are removed for weighting after cooling before decoking. The rate of coking is expressed as weight of coke per unit surface area of the sampler per unit time. Knowing the ratio of surface areas of coke sampler and coil walls, the total coke yield can be calculated.

EXAMPLE -1

A run was carried out at severity of 840 °C COT and 0.5 stream dilution ratio for 12 hours with naphtha feed of 38-140 °C cut consisted of 76.79% paraffins, 17.33% naphthenes and 5.88% aromatics by weight. Reproducibility of the run was tested by repeating the experiment 4 times. the coking rate was 4.7 g/m²/h.

EXAMPLE -2

Example 1 was repeated for 6,12,13,24 and 48 hours with the same naphtha feed. For all the runs temperature profile is maintained constant throughout. Typical temperature profile of a 48 hours run is shown in Figure 2. Initially the coking rate is high and decreases with time to reach an asymptotic value.

EXAMPLE -3

Accelerated coking run was carried out with pure C₅ fraction containing 52% olefins 46% paraffins and 2% aromatics by weight. Since the C₅ fraction contains 52% olefins, which are precursors for coke formation, the feed was considered for accelerated

coking test to establish coke profile of the coil. The run is continued for 72 minutes. The coking rate was 250 g/m²/h. The experiment was carried out at COT of 820°C and dilution ratio of 0.5 and 0.5 s residence time. The coke samplers used were fresh and not subjected to any decoking.

5 **EXAMPLE -4**

An experiment was carried out for 12 hours with a feed containing 70% Naphtha + 30% C 5 fraction. This run was conducted to have the accelerated coking run with a feed representing naphtha characteristics. The coking rate was found to be 7 g/m²/h.

Based on visual observations, the thickness of coke formed was non-uniform. Variations were found on both the top and bottom part of the samplers. The average rates of coke formation for repeated runs were reproducible. The amount of coke formed on the samplers varied with the location of the sampler in the reactor tube. The residence time of the reactants and hence conversion levels increases in the reactor tube as the distance in the reactor increased. Figure 3 shows the coke profile established from the results of 12 hours runs. The x-axis of the plot is position of coke sampler from coil inlet to outlet, which reflects the residence time and they Y-axis shows the corresponding percentage of coke formed. Two maxima are observed in the coke profile.

The first maxima occurred at the top of second pass i.e. at lower residence time. This higher coke formation at low residence times is caused by (1) catalytic reactions on surface wall and (2) free radial reactions of micro species with the free radicals on the coke surface. The micro species with molecular weights of usually 100 or less are often acetylene, ethylene and other olefins and free radical such as methyl, ethyl, phenyl or benzyl radicals. Acetylene reacts with surface radicals to form aromatic rings and dehydrogenation of these rings results in more coke and more surface radicals that permit further reactions with micro species.

The second maxima occurred at the top of third pass where the temperature was at maximum. This coke is formed from heavier coke precursors. Acetylene also reacts in gas phase to produce various coke precursors. Low molecular weight micro species such as benzene are the initial precursors produced and then sequence of condensation and dehydrogenation reactions occurs in gas phase to produce tar droplets and soot particles.

These tar droplets adhere to the surface, decompose to form hydrogen and coke containing numerous surface radicals.

More coke is formed in general with increase in temperature. However, such increase is found to be limited up to certain conversions. At higher conversions, the feed become depleted, concentrations of coke precursors also begin to decrease. This supports the observation of decrease in coke deposition at the exit of the coil

Testing of sulfur oil as an anti coking additive :

Three sets of experiments were carried out to test the sulfur oil as a coke inhibiting additive.

10 EXAMPLE -5

The first set of runs comprised of a blank run i.e. run without any additive and a run with sulfur oil additive. The naphtha feed was mixed with 30% of C₅ fraction to serve the purpose of accelerated coking experiments because C₅ fraction yields more coke during cracking. Same naphtha was used for all the runs of this set. The naphtha feed composition in wt % is given below.

Density (15 ⁰ C)	0.696 g/cc
	Wt %
n-paraffins	41.71
20 i-paraffins	33.62
naphthenes	17.62
aromatics	7.05

Around 3.5 ml of sulfur oil was added to 100 litres of 70% Naphtha and 30% C₅ feed which amounted to around 144 ppmw of sulfur in combined feed. The cracking temperature was 840⁰C and dilution ratio was around 0.4 for both the runs. Each experiment was carried out for 12 hours. The gas product was analysed for product distribution. Overall material balance of all the runs was very good. The first set of experiments were carried out with coke samplers that were subjected to repeated decoking for around 20 times. The temperature profile was maintained constant for all the runs. The average temperature of all the experiments were almost constant. Around 23.5% reduction in coke formation was observed with sulfur oil additive.

EXAMPLE 6

The second set of runs comprised of a blank run i.e. run without and additive, a run with sulfur oil additive and a run with commercial sulfur additive. The second set of experiments were conducted with a new set of coke samplers for all the three runs. Each experiment was carried out for 12 hours. After cooling of the furnace, the coke deposited on the coke samplers was measured. Each run was followed by a decoking run. The feed stock used was.

Density (15 °C)	0.682 g/cc
Wt %	
n-paraffins	37.14
i-paraffins	37.91
naphthenes	17.80
aromatics	7.15

The experiments were conducted at a dilution ratio of 0.45 and COT of 840 °C. The second set of experiments were to compare the sulfur oil performance with commercial sulfur additive. The coke reduction with sulfur oil additive with respect to blank run was 36%, which was similar to commercial additive.

EXAMPLE -7

The third set of runs comprised of a blank run i.e. run without any additive, a run with sulfur oil additive and a run with commercial sulfur additive. These runs were carried out with new set of coke samplers for each of the three runs. The experiments were conducted at a dilution ratio of 0.46 of 0.46 and COT of 840 °C. The composition of the naphtha feed used is given below.

Density (15 °C)	0.686 g/cc
Wt %	
n-paraffins	40.77
i-paraffins	35.76
naphthenes	17.33
aromatics	6.14

Around 50-70% reduction in coke deposition was observed with commercial and sulfur oil additives with respect to blank run.

Reduction of surface coke

The results of all the three sets of experiments mentioned in Examples 5,6, and 7 showed reduction in surface coke rate with sulfur oil and commercial sulfur additive. Figure 4 shows the coke profiles of the three runs. The coke profiles of run with sulfur oil additive and commercial additive are similar. Figure 5, a bar graph, shows the relative surface coke rate of the runs with additives under identical conditions with respect to blank run. The figures 4 and 5 clearly indicate the reduction of surface coke rate with addition of sulfur oil and commercial sulfur additive. The sulfur in the feed reduces rate of coking by reacting with metal surface to form metal sulfides and thus passivating the catalytic effect of the reactor walls.

EXAMPLE –8

After completion of the runs of Example 7 the reactor was cooled and spalled coke that collected in the dead space was measured. The spalled coke was collected from dead legs. Figure 6 shows the amount of spalled coke collected for the three runs. The spalling rate is higher for the runs with sulfur oil and commercial sulfur additive compared to blank run. The chemical additives alter the nature of the coke that is formed. Normally in an untreated run the coke is dense and tightly packed. With the additives in the system the coke is softer, less dense and more brittle and flaky. This altered coke adheres to the surface less readily. It will pass through the furnace coils and end up in dead spaces from where it can easily removed.

Product distribution

The product distribution of typical runs under identical conditions is summarized in Table 1. The addition of sulfur oil as in the case of a commercial additive found to have no significant effect on the product distribution.

Table 1: Product distribution

Feed	Blank	Sulfur oil	Commercial Additive
		Yields	

Component		% wt/wt	
Methane	14.11	14.14	14.06
Ethane	2.75	3.19	3.05
Ethylene	30.45	30.64	29.50
Propane	0.47	0.44	0.43
Propylene	14.78	15.58	15.96
Isobutane	0.05	0.07	0.07
n-butane	0.57	0.30	0.55
t-2 butene	0.36	0.33	0.31
1-butene	0.58	0.63	0.61
Iso-butene	1.46	1.69	1.68
Cis-2-butene	2.74	3.14	2.99
Iso – pentane	0.46	0.50	0.48
1,2 butadiene	1.05	1.21	1.25
N-Pentane	2.23	2.00	1.96
Propyne	0.52	0.50	0.46
1,3-Butadiene	4.82	4.49	4.78
H2	1.58	1.9	1.26

EXAMPLE –9

Total sulfur analysis in gas and liquid products: the total sulfur in pyrolysis gas and liquid products of Example 6 and Example 7 was analyzed. The comparison of total sulfur present in the gas and liquid products of run with sulfur oil additive with those of commercial additive and blank run do not indicate presence of any excess sulfur in the gas and liquid product with sulfur oil.

Claims:

1. A process for thermal cracking of hydrocarbons which comprises feeding said hydrocarbon to a pyrolysis furnace and subjecting it to hydrocracking characterized in that
5 from 100-300 ppmw of a additive comprising of sulfur oil which is a mixture of organic disulfides in the carbon number range of C₂-C₄, is added to said hydrocarbon feed and said feed is subjected to cracking at a temperature in the range of 820-855 °C.
2. A method for inhibiting coke formation on the surface and/or coils of a pyrolysis
10 furnace during a hydrocracking process, which comprises adding to the hydrocarbon feed stock, from 100-300 ppmw of sulfur oil which is a mixture of organic disulfides in the carbon number range of C₂-C₄, and subjecting said feed to cracking at a temperature in the range of 820-855 °C.
- 15 3. A method as claimed in claim 1 or 2 wherein said sulfur oil is a low value product from petroleum refinery.
4. A method as claimed in any preceding claim wherein said organic disulfides comprise alkyl disulfides, wherein the preferred alkyl radicals are methyl and ethyl and
20 the typical sulfur content in said sulfur oil is 60%
5. A method as claimed in any preceding claim wherein the sulfur concentration in the feed is between 140 and 150 ppmw.
- 25 6. A method as claimed in any preceding claim wherein said the additive is decomposable at reaction conditions and completely converted in the furnace.
7. A method as claimed in claim 2 wherein said surface and/or coils of a pyrolysis furnace is made of metal being iron or nickel or both.

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8. A method as claimed in any preceding claim wherein said hydrocarbon feed comprises any hydrocarbon or their mixtures that can be cracked for olefins production.

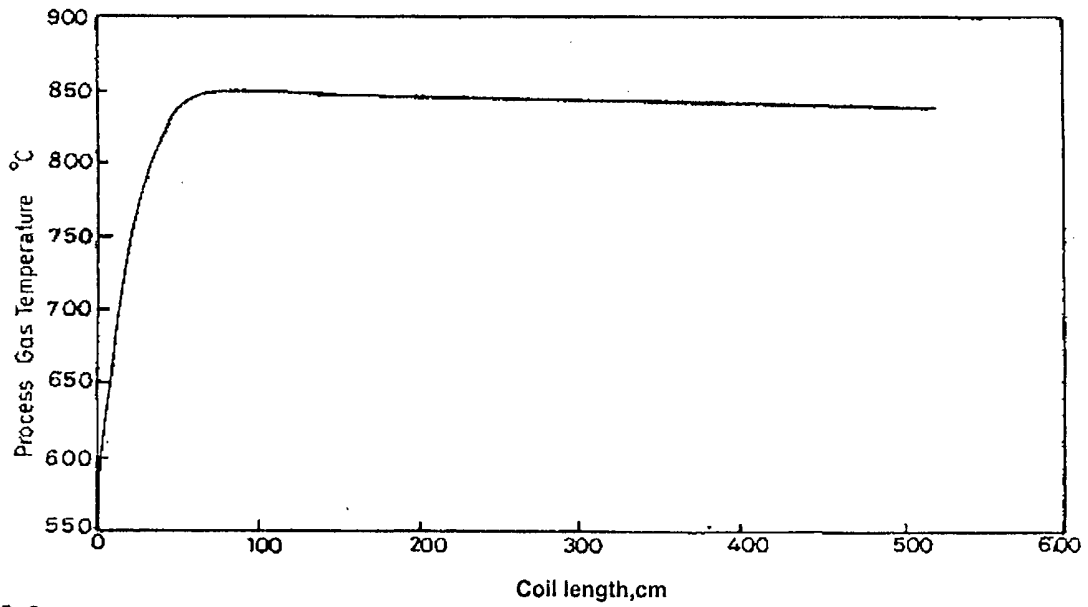
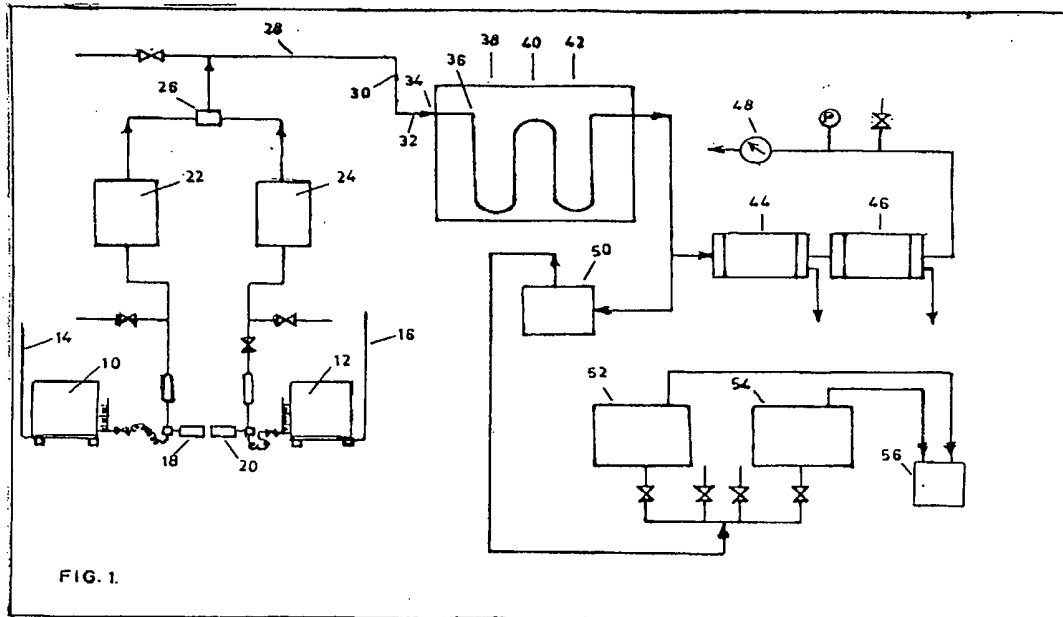


FIG. 2.

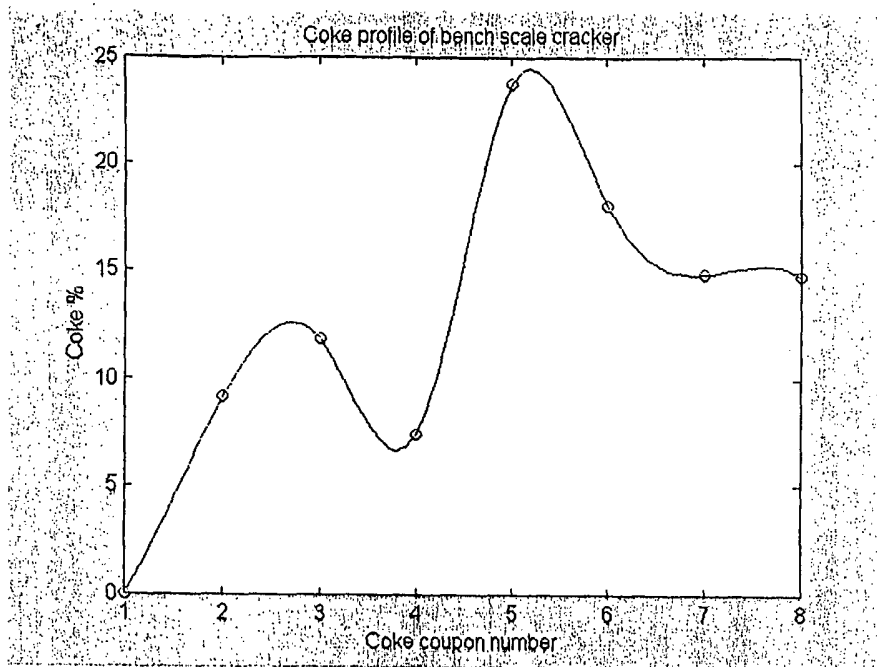


FIG. 3

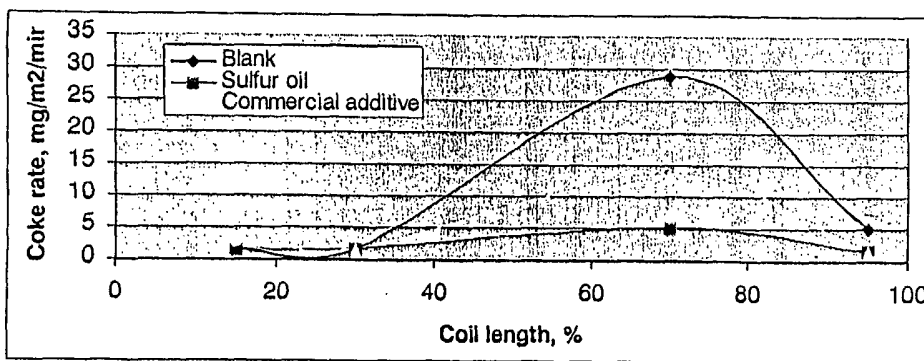


FIG. 4

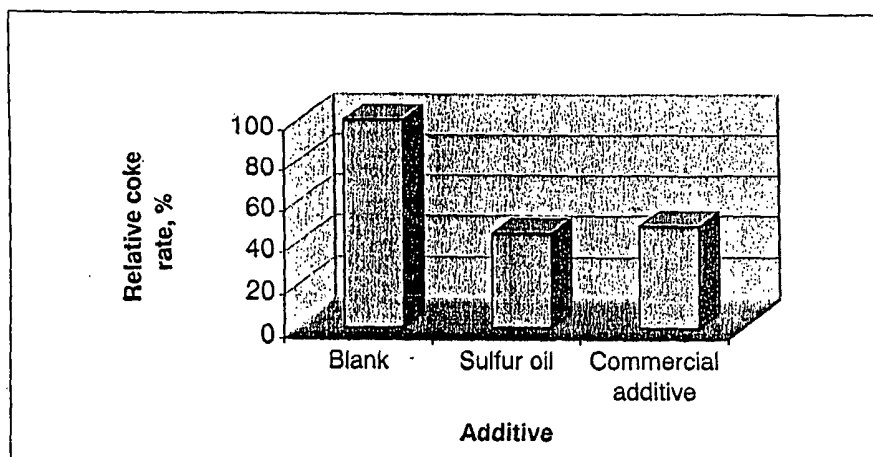


FIG. 5

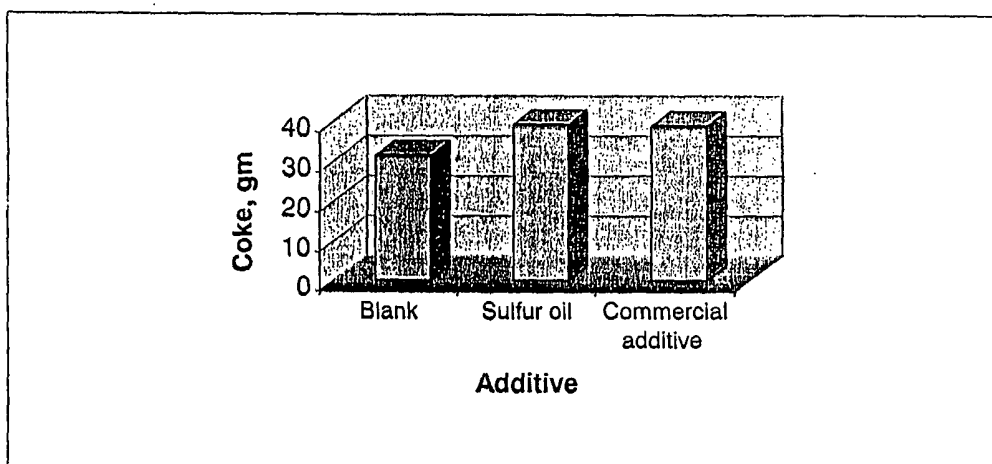


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IN2004/000135

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 7 C10G9/16 C07C4/04 C10G75/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C10G C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 176 186 A (ATOFINA CHEM INC) 30 January 2002 (2002-01-30) the whole document -----	1-8
A	DE 12 34 205 B (METALLGESELLSCHAFT AG) 16 February 1967 (1967-02-16) cited in the application the whole document -----	1-8
A	FR 1 468 873 A (EXXON RESEARCH ENGINEERING CO) 10 February 1967 (1967-02-10) cited in the application the whole document -----	1-8
A	GB 1 090 983 A (EXXON RESEARCH ENGINEERING CO) 15 November 1967 (1967-11-15) cited in the application the whole document -----	1-8
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search	Date of mailing of the international search report	
5 January 2005	24/01/2005	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Cagnoli, M	

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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