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(54) Fuel composition.

(57) A fuel oil composition comprises an oil-in-water emulsion containing 50 to 90% by volume of a sulphur-containing oil having an API gravity in the range 5 to 25° and 50 to 10% by volume of an aqueous solution of an emulsifying surfactant, the oil droplets having a mean droplet diameter in the range 2 to 50 micron. The emulsion additionally comprises a solid sulphur sorbent in the form of solid particles of an alkaline earth metal oxide, hydroxide, carbonate or bicarbonate, the particles having a mean diameter in the range 2 to 50 micron. The sulphur sorbent is present in amount such that the molar ratio of the alkaline earth metal in the solid to the sulphur in the oil is in the range 0.2:1 to 5:1.

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This invention relates to a novel fuel composition comprising an emulsion of a viscous, sulphur-containing oil in water and a particulate sulphur sorbent for reducing the emission of oxides of sulphur when the fuel is combusted.

Low API gravity, viscous crudes are found, for example, in Canada, the Soviet Union, the USA, China and Venezuela. Such materials are characterised as bitumens according to the UNITAR definition of crude oils as defined in the Proceedings of the 1st International Conference on Heavy Crudes and Tar Sands in 1979. These crudes are currently produced either by mechanical pumping, steam injection or by mining techniques. Wide-spread use of these crudes as fuels has been precluded until recently for a number of reasons which include difficulty in production, transportation and handling of the material, and unfavourable combustion characteristics including high sulphur oxide emissions and unburned solids.

Other intractable hydrocarbon substances are the residues from refining operations such as distillation (atmospheric and vacuum), cracking, visbreaking, and other operations. These materials are generally similar in viscosity to the bitumen materials but have a wider range so that some may be less viscous and some may be more viscous. Similar difficulties to those discussed above with respect to bitumens affect their utilisation.

Insofar as transportation and handling of bitumens and residues is concerned these problems have recently been overcome by the technique described in EP 0156486B1. This patent describes and claims a method for the preparation of an HIPR emulsion of oil in water which method comprises directly mixing 70 to 98% by volume of a viscous oil with 30 to 2% by volume of an aqueous solution of an emulsifying surfactant or an alkali, percentages being expressed as percentages by volume of the total mixture; characterised by the fact that the oil has a viscosity in the range 200 to 250,000 mPa.s at the mixing temperature and mixing is effected under low shear conditions in the range 10 to 1,000 reciprocal seconds in such manner that an emulsion is formed comprising highly distorted oil droplets having mean droplet diameters in the range 2 to 50 μm separated by thin interfacial films.

The so-formed HIPR emulsion can then be diluted with an aqueous phase to a desired viscosity or concentration.

The problem of sulphur oxides emission remains, however, and, where there is a need to reduce emissions, this is currently dealt with by treatment during or after combustion.

One method for reducing the emission of oxides of sulphur involves injecting limestone into the combustion furnace. The limestone reacts with the sulphur oxides to form solid calcium sulphate particles which are removed from the flue gases by conventional particulate control devices.

Another method involves flue gas desulphurisation wherein calcium oxide and water are mixed with the flue gases from the furnace.

Both of these methods are expensive and involve the use of special equipment for injecting the sulphur sorbent into the furnace or flue gas stack.

We have now discovered a novel fuel composition in which a solid sulphur sorbent is incorporated into the fuel itself and not injected separately.

Thus according to the present invention there is provided a fuel oil composition comprising an oil-in-water emulsion containing 50 to 90 %, preferably 60 to 75%, by volume of a sulphur-containing oil having an API Gravity in the range 5 to 25°, and 50 to 10%, preferably 40 to 25%, by volume of an aqueous solution of an emulsifying surfactant, percentages being expressed as percentages of the total volume of the liquid phases, the oil droplets having a mean droplet diameter in the range 2 to 50 micron, preferably 5 to 30 micron, characterised by the fact that the emulsion additionally comprises a solid sulphur sorbent in the form of solid particles of an alkaline earth metal oxide, hydroxide, carbonate or bicarbonate, the particles having a mean diameter in the range 2 to 50 micron, preferably 5 to 30 micron, and being present in amount such that the molar ratio of the alkaline earth metal in the solid to the sulphur in the oil is in the range 0.2:1 to 5:1, preferably 0.5:1 to 3:1.

Insofar as the size of the solid particles is concerned, it is necessary to strike a balance between conflicting requirements. Since sulphur capture is related to surface area, and smaller particles have a larger surface area per unit mass than larger ones, it would appear that very small particles would be the most efficient. However, we have found that although very small particles, eg below 5 micron in size, adsorb sulphur more easily, they also desorb more readily at higher temperatures and lose stability at temperatures in excess of 1100°C. Furthermore very small particles are more prone to deposit on heat transfer surfaces and they are more expensive to produce.

Somewhat larger particles, although their initial sulphur uptake is less, are still effective sulphur sorbents, are more stable, are less likely to form deposits on heat transfer substances and are less costly.

With the above constraints in mind, the particle size of the solid sulphur sorbent should be similar to that of the oil droplets.

Suitable sulphur sorbents include calcium hydroxide, magnesium carbonate and magnesium oxide.

The preferred sulphur sorbent is calcium carbonate.

Suitable calcium carbonate particles with a particle size in the range 2 to 50 micron may be obtained as a by-product from the China clay industry or may be obtained by grinding.

The degree of monodispersity of the emulsion is preferably such that at least 60% of the volume of the oil droplets have a droplet diameter within ± 70%, most preferably with ± 30%, of the mean droplet diameter.

The emulsion is preferably prepared by the method disclosed in EP 0156486B1.

If the viscosity of the oil at the emulsification temperature is above 200 mPa.s it will generally be found more convenient to use a two stage process, ie emulsification followed by dilution, to produce emulsions suitable for combustion. If the viscosity of the oil is below 200 mPa.s then a one stage process, ie emulsification with no further dilution, will usually suffice.

In a two stage process the concentration of oil in the first stage emulsion is preferably in the range 80 to 95% by volume and may be diluted to 60 to 75% in the second stage emulsion.

Suitable oils for emulsification include atmospheric and vacuum distillation residues and cracked, visbroken and other residues.

Other oils which can be emulsified include the viscous crude oils to be found in Canada, the USA, Venezuela, and the USSR, for example, Lake Marguerite crude oil from Alberta, Hewitt crude oil from Oklahoma, and Cerro Negro crude oil from the Orinoco oil belt.

Emulsifying surfactants may be non-ionic, ethoxylated ionic, anionic or cationic, but are preferably non-ionic.

Suitable non-ionic surfactants are those whose molecules contain a hydrophobic, hydrocarbyl group and a hydrophilic, polyoxyalkylene group. The latter preferably contains 9 to 100 ethylene oxide units. The preferred non-ionic surfactants are ethoxylated alkyl phenols containing 15 to 45 ethylene oxide units per molecule which are inexpensive and commercially available.

An ethoxylated nonyl phenol containing about 20 ethylene oxide units is very suitable. Single surfactants are suitable and blends of two or more surfactants are not required.

The surfactant is suitably employed in amount 0.5 to 5% by weight, expressed as a percentage by weight of the aqueous solution.

The droplet size can be controlled by varying any or all of the three main parameters: mixing intensity, mixing time and surfactant concentration. Increasing any or all of these will decrease the droplet size.

Emulsification can be carried out over a wide range of temperatures, eg 20° to 200°C, the temperature being significant insofar as it affects the viscosity of the oils. Emulsification will generally be effected under superatmospheric pressure because of operating constraints.

Emulsions of highly viscous fuel oils in water are frequently as much as three to four orders of magnitude less viscous than the oil itself and consequently are much easier to pump and require considerably less energy to do so. Furthermore since the oil droplets are already in an atomised state, the emulsified fuel oil is suitable for use in low pressure burners and requires less preheating, resulting in further saving in capital costs and energy.

Fuel oil emulsions according to the present invention are of uniform high quality and burn efficiently with low emissions of both particulate material and NO_x and lower emissions of SO_x. This is an unusual and highly beneficial feature of the combustion. Usually low particulate emissions are accompanied by high NO_x or vice versa. With a proper burner and optimum excess air the particulate emission can be reduced to the level of the ash content of the fuel whilst still retaining low NO_x emissions.

It is believed that this is a result of the small droplet size and high monodispersity of the emulsions and the presence of water.

The reductions in SO_x are similar to those from existing direct sorbent injection systems with the added advantage that no direct sorbent injection equipment is required, since the sorbent is directly incorporated into the fuel.

The solid waste formed can then easily be collected in conventional equipment. Thus, where sulphur dioxide emissions must be reduced, additional flue gas desulphurisation is not required to burn the fuel, which will be attractive to small users for whom any significant changes to plant are often uneconomic and unwelcome.

Sulphur sorbents in emulsion fuels may prove useful where a small reduction in SO_x is needed to "polish" the flue gas to meet regulations.

The most important parameters affecting the combustion of the emulsion, apart from the quality of the emulsion itself, are the type of burner employed, the quantity of excess air used and possibly the nature of the combustion chamber.

Suitable burners include those using atomisers in which steam, air or fuel gas is used as the atomising fluid.

Suitable quantities of excess air are in the range 1-50%, preferably 2-20%.

In order to maintain optimum combustion characteristics it is necessary that the emulsion remains water continuous until atomisation. In effect, this means that the emulsion should not be over-heated, should not be subjected to high temperatures for long periods and should not be oversheared.

The invention is illustrated with reference to the following examples and the accompanying drawing which shows SO_x profiles for calcium carbonate sulphur sorbents in emulsion fuels.

Example 1

The combustion of emulsion fuels was studied in a Drop Tube Furnace (DTF). This is an electrically heated laminar flow reactor in which the combustion of the fuel spray can be followed as a function of time under a wide range of conditions.

The fuel used was an oil-in-water emulsion containing an initial oil phase ratio of 85:15, before being subsequently diluted down to 70:30 prior to use. The emulsion was prepared by the method disclosed in EP 0156486B1. The base oil was LIFO, (Lavera Inland Fuel Oil), a refinery residue fuel oil, and an analysis of LIFO is given in Table 1. The stabilising surfactant was a non-ionic nonyl phenol ethoxylate containing approximately 20 ethoxy groups per molecule present in the final emulsion at 0.44% wt/wt. The emulsion had a mass mean droplet diameter of 8µm and was stable during atomisation. The base fuel used as a comparison for the sorbent tests was a 70:30 LIFO emulsion prepared by the same method. The test fuels were made up by adding the calcium carbonate to the dilution water used to prepare the 70:30 test emulsion from the 85:15.

The first test emulsion contained 14.4% wt of 5µm calcium carbonate. The sulphur content of the fuel oil was 3.01% wt so the emulsion as fired had a Ca:S molar ratio of 2.75:1. The second test emulsion contained 10.1% wt calcium carbonate with a particle diameter of 25µm. This had a lower calcium to sulphur molar ratio of 1.8:1. The flow rate of emulsion was maintained at a level that gave an oil equivalent of 3.5 g/min. The furnace temperature was set at 900 °C, whilst the total combustion air was kept constant at 15 and 11 1/min at 1.72 bar(g) respectively. A further experiment was carried out at 1100 °C to investigate the effect temperature had on the performance of the coarser calcium carbonate particles.

Gas analysis measurements were taken for SO_2, CO, NO_x and CO_2 at 2% oxygen in the exhaust. Measurements of the gaseous emissions were made between 150 and 1500 ms residence time and solids were collected at a residence time of 1500 ms using a cyclone and analysed by SEM, Malvern particle size analysis and XRF. The results are given in Table 2.

The solids were placed in a thermobalance at 1200 °C for 30 min to show if the sorbent had been fully calcined on its passage through the DTF. The results are given in Table 3.

The experimental results for the measurement of SO_2 levels in the exhaust at different residence times in the DTF are displayed in Figure 1. The SO_2 levels in the exhaust varied from 270 to 1950 ppm depending on the physical form of the sorbent and the experimental conditions. The predicted SO_2 emission, assuming complete combustion and oxidation of the fuel sulphur, was 1980 ppm. The base emulsion SO_2 emissions correspond with this predicted level showing that combustion, and hence SO_2 evolution, is essentially complete within 200 ms.

The measured SO_2 levels for the 5µm $CaCO_3$ particles rose from 270 to 620 ppm as the residence time increased from 160 to 1350 ms. It therefore appears that the SO_2 is initially adsorbed but then desorbed from the sorbent during the remainder of the passage through the furnace. It was not possible to carry out a complete sulphur balance. However, samples of the collected ash as shown in Table 2 contained 21 mole % of the calcium as sulphate. This measurement of bound sulphur and the emitted SO_2 gives a good sulphur balance which implies that relatively little SO_3 was formed. At the exit of the DTF the overall sulphur retention was 66% which is a good result in comparison with other direct sorbent injection systems. Thus the calcium utilisation is good which is a reflection of the very small size of the sorbent particles. If all of the sulphur initially trapped at 160 ms had been retained in the sorbent, then the retention would have been 86% which shows the potential benefits of preventing SO_2 desorption later in the combustion process.

Unfortunately the adverse effect particles of this size have on ash deposition may prevent the use of sorbent particles of this size in certain circumstances. To overcome this problem, work was carried out on larger calcium carbonate particles of 25µm in diameter. The Ca:S ratio was also decreased so the sorbent could be utilised more efficiently. At 900 °C the SO_2 levels rose from 1350 ppm to a mid furnace level of 1500 ppm and decreased to a final level of 1000 ppm at the end of the furnace. This indicates that the sorbent is moderately effective early in combustion but gradually becomes more effective from about 800 ms into combustion. It is possible the calcium carbonate has not completely calcined until this point in the furnace, releasing the calcium oxide at a later stage in the process. Another possibility is that the sorbent fragments with time providing an increasingly greater surface area for adsorption to take place. A mean particle size diameter of 19µm for the ash particles would suggest that the particles have fragmented somewhat as their original size was 25µm.

At 1100°C the SO_2 levels drop erratically from 2000 ppm to 1300 ppm. At this temperature the calcium carbonate should have completely calcined in the first 200 ms of combustion. This suggests that the flame temperature is too high for significant adsorption and it is not until the sorbent is further down the furnace that adsorption can take place. The sorbent reactivity is highly dependent on the peak particle temperature, and if it rises too high the sorbent loses its reactivity or 'deadburns'. Again a mean particle diameter of 19µm suggests there is a possibility that the particles fragment in the DTF.

Samples of the collected ash from the 25µm calcium carbonate particles at 900 and 1100°C had respectively 10 and 5% of the calcium as sulphate. This is in comparison with the 900 and 1100°C reductions of 50 and 30% in SO_2 emissions at the exit of the DTF. The lower temperature conditions appear to be more effective in absorbing SO_2.

To ensure the sorbent had fully calcined in the DTF the ash samples were heated in the thermobalance at 1200°C for 30 min. Any calcium carbonate still remaining would be indicated by a mass loss as it decomposes. The results given in Table 3 show that nearly all the sorbent had calcined in the DTF.

TABLE 1

INSPECTION DATA ON FUEL OILS			
		LIFO	Neuhof
Density at 15°C	kg/1	1.0230	0.9933
Density at 60°C	kg/1	0.9928	0.9628
API Gravity	°	6.8	10.8
Kinematic viscosity at 80°C	cSt	109.4	568.6
Kinematic viscosity at 100°C	cSt	45.83	180.0
Sulphur	%wt	3.01	1.1

TABLE 2

SOLIDS ANALYSIS					
SORBENT	TEMPERATURE (°C)	MgO	ELEMENTAL SO_3	COMPOSITION CaO	(% oxide) Fe_2O_3
5µm $CaCO_3$	900 °C	0.8	20.0	66.0	4.4
25µm $CaCO_3$	900 °C	1.9	11.0	82.0	0.3
25µm $CaCO_3$	1100 °C	1.7	5.4	76.0	0.1

TABLE 3

ASH VALUES FROM THE THERMOBALANCE		
SORBENT (°C)	TEMPERATURE (1200 °C)	ASH
25µm $CaCO_3$	900 °C	96.0%
25µm $CaCO_3$	1100 °C	97.5

Example 2

Tests were performed in the Laboratory Combustion Rig (LCR) using Neuhof emulsion fuel dosed with commercially available calcium carbonate powder which had a 5μm mean size (Superfine grade from Ben Bennett Jr Company). The LCR is a 350 kW oil fired combuster in which a gas atomised fuel spray is burnt under conditions similar to those found in an industrial boiler. Inspection data on the Neuhof base oil is given in Table 1. The emulsion was again prepared by the method disclosed in EP 0156486 B1. For the purposes of the tests the sorbent was premixed with water and surfactant to form a slurry and then dosed into an 85:15 oil/water emulsion to give a final calcium to sulphur molar ratio of 1:1 and 30% water.

Tests were performed over a range of conditions of thermal loading and flue gas excess oxygen. Solids samples were taken in order to estimate the level of sorbent utilisation whilst the reduction in flue gas SO_2 was measured using conventional analysers.

The fuel/sorbent mixture was found to burn with no difficulty of ignition or flame stability. Table 4 summarises the results. For the range of conditions tested it can be seen that the SO_2 reduction achieved was 50% or greater in most cases. In the lowest excess oxygen (0.6%) case the reduction was lower (39%) and this was probably due to the higher flame and exhaust gas temperature.

TABLE 4 - SO_x REDUCTION

Emulsion oil/water composition 70:30. Emulsion volume median drop size - 12 μm. Sorbent volume median particle size - 5 μm microns.

Thermal Input kW	Excess Oxygen % dry	Theoretical SO_2 ppm dry	Measured SO_2 ppm dry	SO_2 reduction %	Flue solids g/m³ at 15°C dry
360	3.8	611	300	51	0.361
230	4.5	578	200	65	0.356
300	3.8	611	320	48	0.213
327	2.2	679	340	50	1.199
320	0.6	737	450	39	1.534

Claims

1. A fuel oil composition comprising an oil-in-water emulsion containing 50 to 90% by volume of a sulphur-containing oil having an API Gravity in the range 5 to 25° and 50 to 10% by volume of an aqueous solution of an emulsifying surfactant, percentages being expressed as percentages of the total volume of the liquid phases, the oil droplets having a mean droplet diameter in the range 2 to 50 micron characterised by the fact that the emulsion additionally comprises a solid sulphur sorbent in the form of solid particles of an alkaline earth metal oxide, hydroxide, carbonate or bicarbonate, the particles having a mean diameter in the range 2 to 50 micron and being present in amount such that the molar ratio of the alkaline earth metal in the solid to the suphur in the oil is in the range 0.2:1 to 5:1.

2. A fuel oil composition according to claim 1 wherein the emulsion contains 60 to 75% by volume of the sulphur-containing viscous oil and 40 to 25% by volume of the aqueous solution of the emulsifying surfactant.

3. A fuel oil composition according to either of the preceding claims wherein the oil droplets have a mean droplet diameter in the range 5 to 30 micron.

4. A fuel oil composition according to any of the preceding claims wherein the solid particles of the alkaline earth metal oxide, hydroxide, carbonate or bicarbonate have a mean diameter in the range 5 to 30 micron.

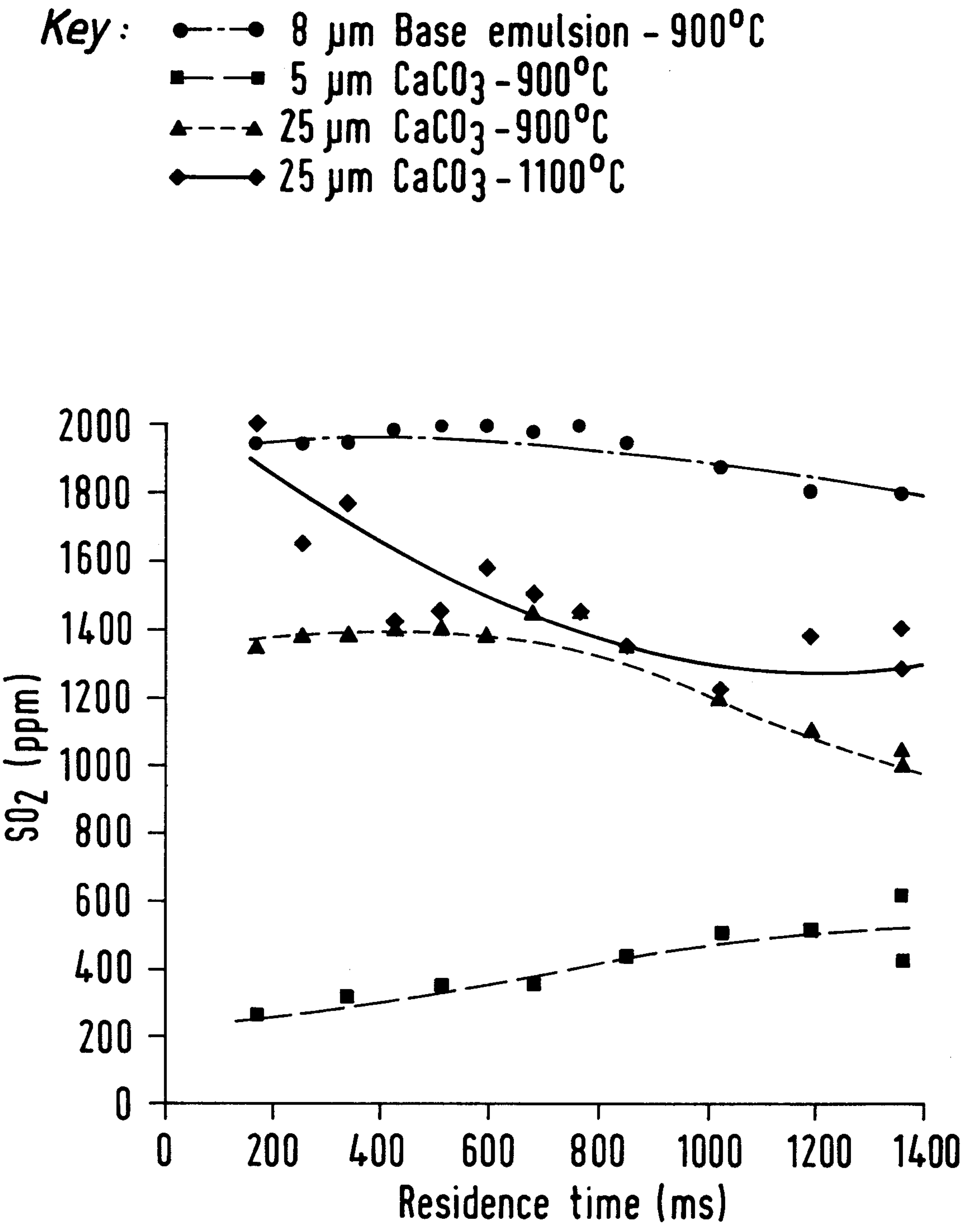
5. A fuel oil composition according to any of the preceding claims wherein the molar ratio of the alkaline earth metal in the solid to the sulphur in the oil is in the range 0.5:1 to 3:1.

6. A fuel oil composition according to any of the preceding claims wherein the solid sulphur sorbent is calcium hydroxide, magnesium carbonate or magnesium oxide.

7. A fuel oil composition according to any of claims 1 to 5 wherein the solid sulphur sorbent is calcium carbonate.

8. A fuel oil composition according to any of the preceding claims wherein the emulsifying surfactant is a non-ionic surfactant.

9. A fuel oil composition according to claim 8 wherein the non-ionic surfactant is an ethoxylated alkyl phenol containing 15 to 45 ethylene oxide groups per molecule.


Key:
●-·-● 8 µm Base emulsion - 900°C
■— —■ 5 µm CaCO3 - 900°C
▲- - -▲ 25 µm CaCO3 - 900°C
◆——◆ 25 µm CaCO3 - 1100°C
SO2 (ppm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
200
400
600
800
1000
1200
1400
Residence time (ms)

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 3758

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WO-A-9 104 310 (PETROFERM)	1,2,4,5, 6,7,8,9	C10L1/32
Y		1,3	
	* claims 1,2,3,5,6,7,8,9,22 * * page 12, line 22 - line 29 * * page 19, line 1 - line 25 * * page 29, line 24 - line 32 * * page 33, line 8 - line 10 * ---		
Y	EP-A-0 301 766 (BP) * claim 7 * -----	1,3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 SEPTEMBER 1992	OSWALD DE HERDT

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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