(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number
WO 02/30553 A2

(51) International Patent Classification⁷: **B01J**

(21) International Application Number: PCT/SE01/02211

(22) International Filing Date: 11 October 2001 (11.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/687,643 13 October 2000 (13.10.2000) US

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(81) Designated States *(national)*: AE, AT, AU, BR, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, HU, ID, IL, IN, IS, JP, LT, MX, NO, NZ, PL, PT, RO, RU, SE, SG, SI, SK, ZA.

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/30553 A2

(54) Title: A PROCESS FOR REDUCING NET GREENHOUSE GAS EMISSIONS FROM CARBON-BEARING INDUSTRIAL OFF-GASES AND A COMPRESSION ENGINE FUEL PRODUCED FROM SAID OFF-GASES

(57) Abstract: Off-gases from metallurgical industry give rise to 10-15 % of all emissions of carbon dioxide in the world. The reduction of the emissions of these off-gases is therefore a key element in any strategy for reducing national or international greenhouse gas emissions. A process for the reduction of net greenhouse gases from industrial off-gases is disclosed, using catalytic processes such as Fischer-Tropsch catalysis. The process has the potential to decrease net greenhouse gas emissions from carbon-bearing industrial off-gases by up to 80-95 % in an economical way. A new type of low-emission fuel for compression engines, in which the main paraffinic component can be manufactured using said catalytic methods, is also disclosed.

A Process for Reducing Net Greenhouse Gas Emissions from Carbon-Bearing Industrial Off-Gases and a Compression Engine Fuel Produced from Said Off-Gases

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Patent references

U.S. Pat. No. 4,678,860 "Process of producing liquid hydrocarbon fuels from biomass", issued 1987-07-07.

U.S. Pat. No. 3,799,520, "Two-part gas collecting hood for converter", issued 1974-03-26.

U.S. Pat. No. 4,007,025, "Apparatus for cleaning stack gas and using same for generation of electric power", issued 1977-02-08.

U.S. Pat. No. 4,052,042, issued 1977-10-04.

U.S. Pat. No. 4,123,238, "Flow-control nozzle for flue-gas scrubber", issued 1978-10-31.

U.S. Pat. No. 4,145,193, "Apparatus for cleaning stack gas and using same for generation of electric power", issued 1979-03-20.

U.S. Pat. No. 4,152,123, "Gas-cleaning apparatus and method for high-pressure blast furnace", issued 1979-05-01.

U.S. Pat. No. 4,153,426 "Synthetic Gas Production", issued May 8th, 1979

U.S. Pat. No. 5,504,118 "Process for the Production of Hydrocarbons", issued April 2nd, 1996

U.S. Pat. No. 4,499,209 "Process for the Preparation of a Fischer-Tropsch catalyst and Preparation of Hydrocarbons from Syngas", issued February 12th, 1985

U.S. Pat. No. 5,844,006 "Process for Producing Liquid and, Optionally, Gaseous Products from Gaseous Reactants", issued December 1st, 1998

U.S. Pat. No. 4,415,142 "Apparatus for handling converter gas", issued Nov. 15, 1983

U.S. Pat. No. 4,218,241 "Method of Recovering Energy from Converter Exhaust Gases", issued

Other references

Schaberg, P., Myburgh, I.S., Botha, J.J., Roets, P.N., Vil-joen, C.L., Dancuart, L.P. and Starr, M.E., "Diesel Exhaust Emissions Using Sasol Slurry Phase Distillate Fuels", SAE Paper 972898, 1997.

Martin, B., Aakko, P., Beckman, D., Giacomo, N.D., and Giavazzi, F., "Influence of Future Fuel Formulations on Diesel Engine Emissions- A Joint European Study", SAE Paper 972966, 1997.

Chandler, K., Norton, P. and Clark, N., "Alternative Fuel Truck Evaluation Project- Design and Preliminary Results", SAE Paper 981392, 1998.

Norton, P., Vertin, K., Baily, B., Clark, N., Lyons, D., Goguen, S., Eberhardt, J., "Emissions from Trucks using Fischer-Tropsch Diesel Fuel" SAE Paper 982426, 1998.

Atkinson, C. M. et al., "In-Cylinder Combustion Pressure Characteristics of Fischer-Tropsch and Conventional Diesel Fuels in a Heavy Duty CI Engine. West Virginia University." SAE Technical Paper No 991472, 1999

Heywood, J. B., "Internal Combustion Engine Fundamentals", McGraw-Hill Book Company, 1988

"Ullman's Encyclopedia of Industrial Chemistry", 5th edition, vol. 12, chapter 4, pages 214-237

TITLE

A Process for Reducing Net Greenhouse Gas Emissions from Carbon-Bearing Metallurgical Off-Gases and a Compression Engine Fuel Produced from said Off-Gases

DESCRIPTION

Technical Field

The present invention relates to a process for reducing net greenhouse gas emissions from carbon-bearing industrial off-gases and a compression engine fuel produced from said off-gases.

Background – Field of Invention

This invention relates to the reduction of emissions of greenhouse gases, and specifically to the reduction of net emissions of carbon-bearing gases from metallurgical industries, and to a fuel for compression engines produced from said carbon-bearing gases.

Background – Prior Art of handling off-gases from metallurgical industry

Off-gases from metallurgical industry, such as blast furnace gas, coke oven gas, basic oxygen furnace gas, and aluminum smelter gas, often contain carbon-bearing gases, such as carbon monoxide and carbon dioxide.

Carbon dioxide is a main contributor to the greenhouse effect, and is estimated to represent some 70% of the total global greenhouse gas emissions. Carbon-bearing gases, such as carbon monoxide, will form carbon dioxide in the atmosphere, and thereby contribute to global warming.

The metallurgical industry emits some 10-15% of the total global emissions of greenhouse gases, and is therefore a key element in any international strategy for abatement of the greenhouse effect.

The handling of metallurgical plant gases and especially the gases produced in steel-making plants is a well developed art and reference may be made, in this connection, to the following U.S. Pat. Nos. 3,799,520, 4,007,025, 4,052,042, 4,123,238, 4,145,193, 4,152,123, 4,218,241, 4,415,142.

Originally, off-gases from metallurgical industries were emitted directly to the surrounding environment from a chimney. Direct emission does not address the emission of greenhouse gases, which is the object of the present invention Direct emission from a chimney has the disadvantage that toxic and corrosive substances, such as carbon monoxide and sulphuric acid, may be emitted without combustion, and also that there is a risk of accidental explosions, should the limit of combustion be reached at any time.

If the gases were above the threshold of combustibility, the off-gases could be burned in a flare. Flaring does not decrease the emission of greenhouse gases, which is the object of the present invention The operation of a flare gives rise to noise and emissions of nitrous oxides, and other solutions have therefore been sought.

In some industries, it was early recognized that energy-rich gases could be used to generate heat or steam for use in the works. A natural extension of this was also to use the gases for production of steam that was subsequently used in adjoining industries and district heating systems.

A further development was made when it was realized that the off-gases could be used in town gas systems. Though steam production and town gas production utilize some of the energy of the gases, it was found in many places that the local demand for heat, steam, and gas was limited, the efficiency often low, and an energy form which could be distributed beyond the local market was sought.

Using the gases for electricity generation using a steam turbine was the next step in the development. However, industrial off-gases are often only available in limited quantities. An estimated 50-80% of the sources are smaller than 200 MWh power per year. Thus, many of the point sources are too small to warrant the building of a steam turbine. The efficiency of a typical steam turbine is only in the range of 25-35%.

Gas turbines are often impractical to use on off-gases from heavy industries, since the off-gases are often contaminated with dust, particles, or sulphur. When used, gas turbines tend to get very expensive both in terms of investment costs and in terms of maintenance costs.

Of course, non-combustible gases cannot be used in any kind of turbine. Since combustion is necessary for the use of a turbine, the emission of nitrous oxides is in practice very difficult to avoid when using a turbine. Nitrous oxides can be reduced using various catalysts, but this will always come at an investment cost, and a cost in terms of lower total efficiency.

The production of chemicals from the off-gases using catalytic processes will avoid the emission of nitrous oxides, as well as any other combustion products. Catalytic processes are often more efficient, giving a higher total energy efficiency. However, prior art approaches to producing chemicals using catalytic methods from metallurgical off-gases have largely been failures, usually due to the fact that too big, too complicated, or too sensitive technology has been applied. For industrial off-gases technology that is suitable in a small scale, conceptually simple, and insensitive to contamination of the gases must be used.

The production of methanol and ammonia from industrial off-gases has been suggested in prior art, i.e. U.S. Patent 4,013,454 and Japanese application 03240907. However, the production of methanol and ammonia is only economically viable in much bigger scale than the scale available from industrial off-gases. The commercial catalysts for methanol and ammonia synthesis are also very sensitive, especially to sulphur contamination, and the gas cleaning before synthesis using industrial off-gases is therefore extremely costly.

The key to successful economic utilization of industrial off-gases for production of chemicals is to realize that the bulk of industrial off-gases are available only in small point-sources. Therefore, economic utilization of the off-gases should preferably be directed towards niche markets for chemicals, where competing production facilities are in the same order of magnitude. This key was not understood by those proposing ammonia and methanol production, since these are extreme bulk markets, with a production of several million tons per year of each substance, and competing plants therefore very big.

Carbon monoxide separated from steelworks off-gases is successfully used in Japan by Kobe Steel for the production of polycarbonate and polyurethane polymers. However, the demand for this application is small, and producing polycarbonate or polyurethane polymers from off-gases will therefore not yield any nationally nor globally significant decrease in greenhouse gas emissions. The method also fails to take advantage of the hydrogen content of the off-gases. Nevertheless, this example shows that chemical production plants utilizing industrial off-gases can be competitive, providing that competing production plants are not several orders of magnitude bigger.

There is a large number of patents on the addition of carbon-bearing material not necessary to the industrial processes, and subsequent use of the off-gases for the production of chemicals, e.g. U.S. Patents 4,132,546, 4,652,307, 4,529,440, 5,714,132, 4,917,727, 4,406,695, and Australian patent 582897. However, the objective of the present invention is to decrease the emissions of carbon-bearing gases, and all additions of carbon-bearing substances not absolutely necessary for the industrial process is therefore highly detrimental to this purpose.

Background - Prior Art of Low-Emission Fuels for Compression Engines

For compression engines, several approaches have been proposed in order to decrease environmental impact from engine emissions. However, they all suffer from limitation of technical, economic, or environmental nature. Generally, the approaches can be divided into new fuel formulations and additives to conventional fuels.

New fuel formulations include re-formulated diesels, rape-seed ester (RME) and di-methyl-ether (DME).

The cleanest standard re-formulated diesel in the world is Swedish diesel “MK1”. Though Swedish MK1 shows a dramatic decrease in toxicity of emissions compared to standard European or U.S. diesel, a significant amount of toxic substances, such as polyaromatics, will nevertheless be emitted. MK1, which is manufactured from crude oil, does not address greenhouse gas emissions at all.

The manufacture of MK1 is relatively energy-intensive , actually yielding higher net emissions of carbon dioxide from the production per kWh than standard European or U.S. diesels.

MK1 is known to cause wear of diesel fuel pumps, and the addition of synthetic lubricity improvers is therefore necessary.

RME, made from rape-seed oil, is well known from prior art. Older engines will need to be converted for use of RME, the production costs of RME are relatively high, and it is known that the emissions have some mutagenic capacity [2]. The need for artificial fertilizers and pesticides, as well as the high usage of area for the culture of rape, contribute to giving RME environmental as well as economic disadvantages. The cold flow properties of RME makes it unsuitable for use in arctic climates.

Methylated esters can be manufactured from many other natural triglycerides, such as soy-bean oil, sunflower oil, or even beef fat. However, all of them share some of the disadvantages of RME.

DME is a relatively clean fuel, with small emissions, but it is considerably more expensive to manufacture than conventional fuels. DME is a gas, and conversion of vehicles is therefore necessary in order to use the fuel. Only a few experimental vehicles are currently run on DME, and there are still technical problems with the engines.

Many additives used in diesel can also be used in the paraffinic fuels of the present invention, additionally decreasing emissions. Thus, oxygen-containing additives, such as water (usually used with an emulgator), ethanol and PEG, are in no competition to the present invention.

Fuels consisting mainly of ethanol or methanol are not possible to use efficiently in compression engines, and are therefore not in competition to the present invention.

Bio-gas (methane from fermentation processes) is used in Otto engines, and is therefore not in competition to the present invention. Compression engines have a much higher efficiency than Otto engines – around 30-50% difference is not uncommon in commercial vehicles. Thus, limited fuel resources, in the form of clean fuels, can be used more efficiently in compression engines than in Otto engines.

There have been several indepth investigations of Fischer-Tropsch fuels, e.g., U.S. Patent 6,056,793. However, in these other investigations, the optimum molecular composition that will allow consistently improved results compared to Swedish MK1 diesel were not described.

Objects and Advantages

Accordingly, several objects and advantages of the present invention are:

(a) to provide for the efficient utilization of 70-90% of the energy contained in the off-gases;

(b) to provide for total carbon capture ratios of 80-95%, and thereby a reduction of greenhouse gas emissions by 80-95%;

(c) to provide for the use of catalysts that are inexpensive and insensitive;

(d) to provide for the efficient utilization of carbon monoxide, carbon dioxide, hydrocarbons, and hydrogen in the off-gases;

(e) to provide synthesis gas for the production of high-value hydrocarbons, such as specialty vehicle fuels, waxes, and lubricants;

(f) to provide for the economic operation of the plant, since competing plants are not much bigger;

(g) to provide for the production of chemicals with a high energy content per unit volume, thereby allowing the economic transport and distribution of the energy contained in the chemicals to distant places;

(h) to provide for the economic recovery of sulphur-free carbon dioxide to be used in demanding applications, such as food products;

(i) to provide for the production of environmentally compatible and highly functional compression engine fuels, with lower emissions than any current commercial compression engine fuel;

(j) to provide for a method of catalytic carbon capture that will emit no toxins or respiratory irritants;

(k) to provide for the economic utilization of modern catalytic technology in a relatively small scale. This is made possible by:

– the limited need for pre-treatment of the raw material - synthesis gas is readily available in many industrial off-gases. A relatively inexpensive shift operation that converts carbon monoxide and steam to hydrogen and carbon dioxide may sometimes be needed before passing on the gas to the catalysis reactor.

– the limited need for after-treatment - a relatively inexpensive hydrogenation step can produce low-sulphur naphtha, diesel, and wax/lubricant. Since no gasoline is produced, no expensive isomerization equipment is needed.

– a premium can be charged for fuels and chemicals that are essentially free from aromatic substances. Aromatics, such as xylene, benzene, and bens(a)pyrene, are usually toxic. Many are also carcinogens or allergens. In many products, they must therefore be meticulously avoided, something which is very costly to achieve in an ordinary crude oil based refinery.

Further objects and advantages of the present invention will become apparent from a consideration of the ensuing descriptions and drawings.

Drawing Figures

Figure 1 shows one embodiment of the invention using the off-gas from a basic oxygen furnace of a steelworks.

Reference Numerals in Drawing

10 basic oxygen furnace

12 valves

14 gas storage tank

16 compressor

18 Shift reactor

20 CO2 separation

22 Fischer-Tropsch reactor

24 settling and aftertreatment

26 hydrocarbons

28 flare

30 carbon dioxide holder

Description – Figure 1

Figure 1 shows one embodiment of the present invention. The off-gas is in this case generated from a basic oxygen furnace 10 of a steel manufacturing plant. The basic oxygen furnace is of a type that has a hood capturing off-gases from the process. The off-gases are passed to a set of valves 12, which will pass on the gas to the next step only if the carbon monoxide content of the gas is above an adjustable limit.

Though many different valve constructions can in principle be used, a few examples of basic valve constructions are given in U.S. Patents 4,415,142 and 4,218,241. If the gas does not contain the minimum limit of energy-rich gases, they may be passed to a chimney or flare 28.

The off-gas is passed on to an expandable gas storage tank 14, of a size sufficient to give an essentially steady flow of gas out from the gas container. The pressure of the gas storage tank is kept between approximately 1 and 3 bars. From the gas container, the gas is passed on to a compressor 16, where the gas is compressed to a pressure of approximately 10 to 50 bars.

The compressed gas is passed on to a shift reactor 18. The function of the shift reactor is to convert some of the carbon monoxide of the off-gas to hydrogen, while the high temperature and the catalyst employed will simultaneously destroy any remaining traces of smelly hydrocarbons that may still be present in the gas.

An optional carbon dioxide separation step 20 is included in figure 1. This step is only necessary if there is a use for said carbon dioxide, since all remaining steps will work with or without carbon dioxide in the gas stream. Any conventional method of separation will work, e.g. cryogenic separation, ethanol-amine solvent, or alkaline water wash.

The gas is then passed to the catalytic reactor 22, which in this embodiment is a Fischer-Tropsch reactor utilizing an iron-based catalyst. Many different types of reactors can be used in the present invention, including fischer-tropsch reactors, water shift reactors, inverse water shift reactors, oxo synthesis reactors, and carbonylation reactors. A few examples of Fischer-Tropsch reactors which are all possible to use in the present invention are described in U.S. Patents 5,504,118, 4,499,209, and 5,844,006.

The liquid and gaseous output of the reactor is passed to settling and aftertreatment, 22. This process step consists of settling, hydrogenation, and distillation. In the settling, an oil phase, mainly consisting of C5+ hydrocarbons and alcohols will separate from a water phase, mainly consisting of water, lower alcohols, ketons, and aldehydes.

The oil phase is hydrogenated and distilled into various fractions, e.g. wax, diesel, jet fuel, and naphtha. In the hydrogenation, olefins will be saturated to paraffins, and the distilled fuel will therefore have a very low content of olefins.

The water phase is also hydrogenated, in such a way that ketons and aldehydes are reacted to alcohols. The water phase can then be used as a ion-free cleaning agent, or the alcohols can be distilled out, and sold separately.

Remaining reactive gases from the settling can be flared in the flare 28, or recycled to the gas storage tank 14. However, to avoid build-up of inert gases (mainly nitrogen), a large fraction of the nitrogen must be released through a flare or chimney.

Operation – Figure 1

The off-gases passed on from the basic oxygen furnace 10 will have a high content of carbon-bearing gases only during the blow of oxygen into the steel melt. Thus the valves 12 are adjusted so that only gas containing a pre-determined content of carbon-bearing gas is passed on to the gas storage tank 14.

This pre-determined content of carbon-bearing gas is optimized with regard to the overall economics of the process, depending on conditions such as market value of carbon dioxide. Usually, the valve 12 will be set at minimum of approximately 40-60% carbon-bearing gas.

The typical composition of the off-gas from a basic oxygen furnace gas will be around 65 vol.-% carbon monoxide, around 15 vol.-% carbon dioxide, around 18 vol.-% nitrogen gas, and less than 2 vol.-% hydrogen gas. The off-gas is essentially sulphur-free. The off-gas contains 5-50 mg/Nm^3 dust, mainly ferrous oxides.

In a typical steelworks producing around 1.6 million tons of steel per year, the amount of off-gas will be around 120 million Nm^3 per year. The off-gas is produced during the oxygen blows in the basic oxygen furnace 10, usually around 15 minutes, and then no gas is produced before the next blow, which will usually be a time period of 20 to 30 minutes.

The size of the gas storage tank 14 is chosen to minimize the risk of production stops due to too low gas levels. Thus, the size should be at least as large as the amount of gas produced by one blow, and preferably two or three times the volume of off-gas produced in one blow. This will allow for a steady flow of gas from the gas storage tank 14 to the compressor 16. The compressor 16 will compress the off-gas to approximately10 to 50 bars.

The gas is then passed to the shift reactor 18, in which steam is injected. The steam reacts with the carbon monoxide of the gas, producing carbon dioxide and hydrogen. In an optional carbon dioxide separation unit 20, some of the carbon dioxide may be separated for use in other applications, within or outside the plant.

The catalysis reactor 22, which in this embodiment is a Fischer-Tropsch reactor, will then use the carbon monoxide and hydrogen content of the gas to produce the following end products:

(a) saturated non-cyclic hydrocarbons, e.g. alkanes

(b) non-saturated non-cyclic hydrocarbons, e.g. alkenes

(c) oxygenates, e.g. alcohols, aldehydes, and ketons

(d) water

A residual gas will contain carbon dioxide, hydrogen, and some light hydrocarbons. The products from the reactor are passed on to settling and aftertreatment. From the settler, gases are flared or vented off via the flare 18. A small fraction of the gas may also be recycled to the gas storage tank 14.

In the settling, a phase separation will take place. The water and the water-soluble oxygenates will form a bottom layer in the settler, and the alkanes and alkenes a top layer, which can be skimmed or funneled off from the top of the settler.

The alkanes and alkenes from the settling are passed on to a hydrogenation step, where the alkenes are saturated using hydrogen and a suitable catalyst.

The product from the hydrogenation will consist essentially of alkanes. Lighter alkanes, up to about 20 carbon atoms, can easily be separated using ordinary distillation techniques, whereas heavier alkanes may need to be separated in vacuum distillation or solvent extraction. Since mainly non-cyclic alkanes are produced, no azeotrops will be present in the distillation.

It could be argued that if the hydrocarbons are combusted in an engine, they will nevertheless be emitted, and no decrease in greenhouse gas emissions would be effected. However, there will nevertheless be a net decrease in greenhous gas emissions, since said hydrocarbons would replace fuels that would otherwise be from a fossil source. Thus, care must be taken that the fuels of the present invention are not used to replace non-fossil fuels, since this would not yield a net decrease of greenhouse gas emissions.

Description of a New Low-Emission Fuel Composition for Compression Engines

Two different mixtures of essentially paraffinic fuels with variation in carbon chain branching and, to a certain extent, variation in chain length were tested and their results were compared with those obtained from conventional Swedish fuel of environmental class 1 (MK1). Swedish diesel fuel environmental class 1 is currently the cleanest standard diesel fuel in the world.

The selected optimized paraffinic fuel mixtures were further tested according to the 13 mode ECE R49 test cycle and were found to have lower emissions than MK1 fuel with regard to all measured emissions.

The composition of the fuels were chosen so that they can be manufactured from industrial off-gases using a Fischer-Tropsch catalysis reactor in the production process described in figure 1 and in the above text. However, other manufacturing methods are also possible.

The fuels may also be manufactured from renewable raw materials, e.g. wood chips. The production process in this case is first a partial oxidation of the wood chips, producing synthesis gas. The synthesis gas is passed to a Fischer-Tropsch reactor, and the process thereafter is essentially the same as that described above. For further reference on the thereafter is essentially the same as that described above. For further reference on the production of bio-fuels using Fischer-Tropsch processes, reference is made to U.S. Pat. No. 4,678,860. Other raw materials used in a similar process could be natural gas, sewage sludge, or other types of waste.

The fuels could also be manufactured using traditional refinery technology, using crude oil as the raw material. However, a large number of de-sulphurization, distillation, and purification steps are needed in this case, making Fischer-Tropsch processes more economical in most cases.

TEST FUELS

The fuels were prepared by mixing three different paraffin chemicals. It should be borne in mind that, just as in the case of so-called "diesel" fuel, the designation Fischer-Tropsch fuel (F-T fuel) represents a generic type of fuel, rather than a fixed fuel specification. As a result, there are potentially an infinite number of F-T fuels that each could have their own unique fuel specification.

It is important to note that the fuels produced in Fischer-Tropsch synthesis and ensuing hydrogenation can be designed to be chemically identical to the fuels tested here. Therefore, any emissions will also be chemically identical.

The F-T fuel mixture 1 consist of 90% straight-chain n-paraffins, C10 to C13 in length, which has a high cetane number and rather good lubricity properties but not so good cold flow properties. It was therefore mixed with 10% n-heptane (C_7H_{16}).

The F-T fuel mixture 2 consist of 60% straight-chain n-paraffins, C10 to C13 in length, 20% strongly branched-chain iso-paraffin, C10 to C15 in length, and 20% weakly branched-chain iso-paraffin, C10 to C13 in length. The branched-chain iso-paraffins have slightly lower cetane number and less good lubricity properties but very good cold flow properties compared to straight-chain paraffin.

For reference purpose, MK1 diesel was used. Some data on the fuels are shown in tables 1, 2 and 3 below.

Table 1

Paraffin mixture 1 (FT1 FUEL) :

Test	**Unit**	**Method**	**Result**
CFPP	deg. C	EN 116	minus 25 deg. C
Calorific Value Gross	MJ/kg	ASTM D 240	43.7
HFRR Wear Scar	Micrometer	ISO 12156	883
Cetane Number	--	ASTM D 613	above 70
Density @ 15 deg. C	kg/m^3	ASTM D 4052	744.1
Distillation	--	ASTM D 86	---
IBP	deg. C	ASTM D 86	113.4
Temp. at 10 % rec.	deg. C	ASTM D 86	170.2
Temp. at 50 % rec.	deg. C	ASTM D 86	206.7
Temp. at 90% rec.	deg. C	ASTM D 86	220.9
FBP	deg. C	ASTM D 86	228.5
Residue	vol. %	ASTM D 86	1.4
Flash point (PM)	deg. C	ASTM D 93	33.5 *
Viscosity at 40 deg. C	mm^2/s	ISO 3104	1.218

* Tested with method IP 170. Result = 31.0

Table 2

Paraffin mixture 2 (F-T2 FUEL) :

Test	Unit	Method	Result
CFPP	deg. C	EN 116	minus 33 deg. C
Calorific Value Gross	MJ/kg	ASTM D 240	46.65
HFRR Wear Scar	Micrometer	ISO 12156	885.
Cetane Number	--	ASTM D 613	61.4
Density @ 15 deg. C	kg/m^3	ASTM D 4052	761.4
Distillation	--	ASTM D 86	--
IBP	deg. C	ASTM D 86	195.7
Temp. at 10 % rec.	deg. C	ASTM D 86	201.3
Temp. at 50 % rec.	deg. C	ASTM D 86	208.0
Temp. at 90% rec.	deg. C	ASTM D 86	225.3
FBP	deg. C	ASTM D 86	240.4
Residue	vol. %	ASTM D 86	1.5
Flash point (PM)	deg. C	ASTM D 93	66.0
Viscosity at 40 deg. C	mm^2/s	ISO 3104	1.416

Table 3

Typical properties of Swedish MK1 diesel

Test	**Unit**	**Method**	**Result**
CFPP	°C	EN 116	- 40
Calorific Value Gross	MJ/kg	ASTM D 240	
HFRR Wear Scar	Micrometer	ISO 12156	370
Cetane Number	--	ASTM D 613	53-54
Density @ 15 deg. C	kg/m^3	ASTM D 4052	810-820
Distillation	--	ASTM D 86	--
IBP	deg. C	ASTM D 86	190-195
Temp. at 50 % rec.	deg. C	ASTM D 86	approx 230
Temp. at 95% rec.	deg. C	ASTM D 86	282
FBP	deg. C	ASTM D 86	300
Residue	vol. %	ASTM D 86	1.5
Aromatics	vol. %	IP 391	4,5
Polyaromatics content	vol.-%	IP 391	<0.02
Sulphur content	mg/kg	ASTM D5453	< 1
Water content	mg/kg	ASTM D6304	20-30
Ash content	wt.-%	ASTM D482	<0.001
Flash point (PM)	deg. C	ASTM D 93	70-75
Viscosity at 40 deg. C	mm^2/s	ISO 3104	approx 2

ENGINE TESTING

Test engine

The test engine consists of a basic AVL Type 501 cylinder block and Volvo - 2 l cylinder head. The single cylinder research engine, equipped with C-3 Lucas unit - injector, has the following configuration:

Compression ratio	17.9:1
Bore-Stroke	131-150 mm
Piston swept volume	2,022 l
Engine nominal speed	1800 rpm
Piston bowl	97.73 cm3
Nozzle specification	8x0.22x158 deg
Protrusion	1.4 mm

Turbocharger performance of a six cylinder production engine was simulated by the AVL 5153 supercharging group according to the discrete parameters read from the Volvo test No FP01940865 - 867 - 874 - 876 - 878 - 880. Hence, the engine would run at the same power-speed points and supercharging specifications as in the Volvo tests. Such performance would help to compare the reference results, when the engine runs on conventional fuel MK1, with F-T fuel test results.

The engine cooling water temperature was set at constant value of 85 Celsius degree via the engine water cooling unit AVL 553, whereas the lube oil temperature was set at constant value of 90 Celsius degree via the oil cooling unit AVL 554. The fuel conditioning system used during this investigation was AVL 753 M - 120.

Measuring equipment

The speed-torque engine operating range was controlled by an AVL PUMA engine test system. Such a system includes measuring devices such as: Variable Sampling Smoke Meter AVL 415, Dynamic Fuel Meter AVL 733S, and Exhaust Gas Analytical System CEB series equipped with a Bench Integration Computer BIC. The emission test system was calibrated before the test procedure and it was controlled continuously during the long day test. The regulated emission NOx and HC were measured in ppm at wet conditions, whereas CO and CO_2 were measured at dry conditions. The soot formation was measured in FSN (Filter Smoke Number) units. According to the software program, and device arrangement for constant length of the sampling volume, FSN might be converted to mg/m^3.

The air mass flow was measured by a thermal Air Mass Flow Meter (AFM), which is placed before the inlet of the air filter onto the compressor. After the compressor unit the compressed air is led through a FD 160 Air Drier, where the moisture is removed by cooling the air to near freezing point.

The by-pass Constant Pressure Regulator (CPR) maintains a constant supply pressure of about 5 bar for the boost pressure control group. Further, the Boost Pressure Control Group (BPCG) 5262 provides the requested charging air temperature and pressure for the engine. An accurate Hygrotest 602 instrument with the probe of the humidity measuring transducer directly installed on the steady vessel of the BPCG 5262 was used to measure small quantities of the remaining humidity.

Remote Injection Control and Data Processing

The remote injection program is design to give injection control for timing and duration of the main pulse via a PC. This program is integrated into the existing fuelling strategies. Therefore, the Engine Control Unit (ECU) can be operated in a normal running mode with existing controls or via the remote program which will directly control the injection pulse. In order to define the real timing for injection and its duration, a software for analysis of the combustion and thermodynamics through measurements of cylinder pressure and other fuel injection related variables has been developed under the name *Dragon.*

Thermodynamic analysis also gives a number of parameters that characterizes the combustion processes, such as heat release rate, ignition delay, injection duration and fractions of the premixed-diffusion combustion. A NOx formation model is also implemented, but since the accurate measuring instrumentation is used, this model was not activated. *Burst to File* sampling code sampled the high frequency signals, such as cylinder pressure, fuel pressure, needle lift, and solenoid valve signal. High frequency signals were further processed by the *Dragon* program giving the real values for needle lift and heat release history.

TEST PROCEDURE

Initially, the engine was run on conventional fuel MK1 until the specifications of the engine test point (ECE R49. 13 mode) were reached and remained very stable. Emission concentrations and engine parameters were measured every second during 120 seconds and the average value was recorded by the AVL computer system.

When the adequate information was collected at each step of the ECE test cycle, the fuel system was fed with different F-T fuels mixture. The same procedure as for MK1 fuel was repeated until the engine test point was reached and remained very stable. In the F-T fuels case the two different mixtures were fed into the fuel system and the engine parameters were recorded.

Detailed investigations of organic components in the exhaust were performed using a GC-MS analysis equipment.

EMISSION ANALYSIS.

According to the ECE R49 13-mode test cycle evaluation the specific emission for standard fuel MK1 and F-T fuels Mixture 1 and Mixture 2 are shown in Table 4.

Table 4.

Specific emissions according to the ECE R49 13 mode test cycle.

Emissions	**MK1**	**FT 1**	**FT 2**	FT1-Mk1 %	FT2-MK1 %	Units
NOx	**6.3849**	**5.9755**	**6.0645**	-6.41	-5.02	g/kWh
HC	**0.2693**	**0.2246**	**0.2209**	-16.59	-17.97	g/kWh
CO	**0.9603**	**0.8961**	**0.8527**	-6.69	-11.19	g/kWh
Soot	**0.0493**	**0.0399**	**0.0408**	-19.07	-17.24	g/kWh
bsfc	**236.93**	**236.64**	**234.37**	-0.12	-1.08	g/kWh

As shown, all emissions are reduced almost at the same gradient in comparison to those obtained when the engine runs on standard diesel fuel MK1. F-T fuel mixture 2 shows to have better performance encountering CO and Soot formation, but less effective in NOx reduction.

As a complement to this, it might be interesting to analyze specific emissions versus engine load for the two speeds of the ECE test cycle, 1200 and 1800 rpm.

As might be observed from table 4, F-T fuels have lower emissions than MK1 at all operating points, but more pronounced at light loads. From his viewpoint both mixtures show the same trend. However, the weighted emissions of ECE R49 test cycle (Table 4) for NOx and CO emissions look different for F-T1 and F-T2. F-T1 forms less NOx and more CO in comparison with those emissions obtained when the engine runs on F-T2. Further explanations might be found from cylinder pressure and heat release analysis.

The evaluation of ignition delay, Fig. 2, in CAD at intermediate and rated speed show smaller values for the F-T fuels as compared to MK1 fuel, especially at low load. This is one of the main reasons for lower NOx levels obtained when the engine runs on F-T fuels. Between two F-T fuels, F-T1 seems to have shorter ignition delay.

The detailed emission measurements were collected simultaneously with the measurements reported above. The exhaust gases were sucked through a micro-filter where heavy organic components in the interval C_5 to C_{20} were adsorbed.

A general result for all fuels indicates that the time required to reach stable emissions from the engine system is quite long. When changing the load point, 30-60 minutes running was required to reach stabilization.

None of the fuels produced any new components in significant (measurable) quantity. The exhaust emissions were dominated by fuel components. The ratio between the different components did vary with load. At low load, the fuel composition dominates the exhaust composition while at higher loads the heavier components dominates in the exhaust.

THERMODYNAMIC ANALYSIS

Cylinder pressure was further processed for heat release analysis according to the Dragon software. This program uses an algorithm with the aim of permitting a quick assessment of the combustion process i.e. the heat release and the temperature per degree crank angle and total heat released immediately after the measurement. In order to calculate such parameters, the indicated diagram must range at least from intake valve closed to exhaust valve opened.

This thermodynamic calculation principle compares the measured pressure response with a computed pressure curve making use of the fact that a different pressure rise is observed in the compression phase and in the expansion phase depending on the time when combustion starts and develops.

The heat release rate is defined as the effective portion of combustion energy that is available for heating up the gas in the combustion chamber. Obviously, the computation of surface losses requires a computer algorithm, which has been developed for thermal simulation.

Mathematical formulas for changes in volume, rate of heat release, total heat release, and gas temperature according to the different steps of calculations are not shown here, as they have been described in other publications [Atkinson et al, Heywood].

The most general thermodynamic information when running on different fuels is the engine efficiency. This parameter is evaluated using a lower heat value for the fuels of 42.8 MJ/kg. The only parameter, considered to vary in our investigation, has been the equivalent ratio, which differs for MK1 and F-T fuels. Such difference is compensated during the tests, where the engine was run at the same equivalent ratio. Table 5 shows the engine efficiencies values at different speed and load for conventional fuel MK1 and F-T fuels.

Table 5
Engine efficiencies for different loads and fuels.

Engine efficiency at Intermediate speed =1200 rpm

Load %	10	25	50	75	100
MK1	0.231	0.324	0.358	0.385	0.390
F-T1	0.233	0.325	0.369	0.39	0.391
F-T2	0.237	0.326	0.368	0.39	0.396

Engine efficiency at Rated speed, 1800 rpm

MK1	0.184	0.279	0.331	0.353	0.349
F-T1	0.182	0.278	0.329	0.352	0.342
F-T2	0.183	0.28	0.334	0.351	0.346

Efficiency change in % at intermediate speed

Load %	10	25	50	75	100
F-T1	0.866	0.309	3.073	1.299	0.256
F-T2	2.597	0.617	2.793	1.299	1.539

Efficiency change in % at rated speed

F-T1	-1.087	-0.358	-0.604	-0.283	-2.006
F-T2	-0.544	0.358	0.906	-0.567	-0.860

Generally speaking, at intermediate speed both F-T fuels have shown better performance in comparison with conventional fuel MK1. However, at rated speed the F-T1 fuel exhibits better performance at middle loads.

The rate of heat release (RoHR) shows that the fraction of premixed combustion for conventional fuel (MK1) is much stronger than for the F-T fuels. This is an available information about engine thermodynamics and combustion characteristics, which shows the difference between MK1 and F-T fuels. As might be observed from the diagram, the premixed combustion for F-T2 fuel at rated speed and 75% load is almost undetectable. This would lead to lower combustion temperature, lower combustion rate, smoother engine running, and most importantly to a lower NOx formation speed.

Such deduction is valid almost for each step of the ECE R49 test cycle, therefore we have not shown all of them here.

The evaluation of ignition delay, fig. 2, in CAD at intermediate and rated speed show smaller values for the F-T fuels as compared to MK1 fuel, especially at low load. This is one of the main reasons for lower NOx levels obtained when the engine runs on F-T fuels. Between two F-T fuels, F-T1 seems to have shorter ignition delay.

Table 6.

Peak pressure and its location for MK1 and F-T fuels, 1200 rpm.

Load	Peak pressure [bar]			Peak pressure location [CAD]		
%	MK1	F-T1	F-T2	MK1	F-T1	F-T2
10	58.4	54.1	55.5	10.35	9.37	10.09
25	60.1	59.8	60	14.51	14.22	13.55
50	75.1	75	74	17.64	17.4	17.5
75	91	89.3	91	18.36	16.34	17.23
100	110.7	110.04	111	18.44	18.21	18.3

As shown in Table 6 the peak pressure for MK1 is slightly higher than those for F-T fuels. The peak pressure location is also slightly later for MK1. Higher peak pressure and its later location related to the piston position for MK1 fuel points out the different properties in the combustion characteristics for F-T fuels. Such a trend is hardly observed at rated speed as the peak pressure is located at the compression line (stroke) and not at the combustion line (expansion stroke). Generally speaking, thermodynamic analysis shows that F-T fuels exhibit better performance in comparison with conventional MK1.

Due to some fluctuation in intake pressure, insignificant inconsistency between different parameters for different fuels are observed at a few load points, particularly at rated speed. However, the experimental investigation of F-T fuels impact on diesel engine performance confirm better thermodynamic performance, and lower emission levels.

CONCLUSIONS FROM EMISSION TESTING

Experimental investigation of F-T fuels and their impact on diesel engine performance was done in a single cylinder research engine. Experimental results have shown that F-T fuels have a significant impact not only on the emissions levels, but also on other energetic parameters of the engine such as ignition delay, cylinder peak pressure, heat release gradient, indicated efficiency etc.

The regulated emissions, emitted by the diesel engine when it runs on F-T fuels, are lower than those of conventional MK1 fuel. The ECE R49 13 mode evaluation of specific weighted values have shown a general NOx reduction by 6%, HC reduction by 17%, CO reduction by 10% and Soot reduction by 19%. Insignificant BSFC reduction was observed as well, but not as much as to be stated. At some loads (from light load 10% to medium load 50%) the emission reductions were higher. Hence, NOx reduction reached 25%, HC 50% and CO 30%. Soot formation was observed to be reduced only at loads higher than 50%, and achieved the maximum reduction by 20%.

The detailed measurement of organics showed that none of the fuels produced any significant amounts of dangerous higher organic compounds for example PAH. The emissions were dominated completely by fuel components. The ratios between the fuel alkanes varied with the engine mode studied. For low power modes, such as mode 2, the emissions were dominated by unburnt fuel. For high power modes, such as mode 6 and 8, the concentrations of organics in the emissions were very low and contained more heavier alkanes.

There is only paraffins in the fuels, and there is basically only paraffins in the exhausts. The heavier paraffin fuel components dominates in the exhaust at higher loads. Since there is much more different types of molecules in the F-T2, there is also much more types of molecules in the exhaust with this fuel formulation. No formation of aromatic compounds or PAH has been observed.

Generally speaking, F-T fuels are shown to be effective over the operating range of the engine, and particularly at light loads. From this viewpoint both F-T mixtures show the same trend. However, the general index of ECE R49 test cycles evaluations for NOx and CO emissions is slightly different for F-T1 and F-T2 fuels. F-T1 forms less NOx and more CO in comparison with those emissions obtained when the engine runs on F-T2.

From combustion characteristics point of view, it is observed that F-T fuels have shorter ignition delay and longer combustion duration when compared with those obtained when the engine runs on MK1 fuel at the same operating point. Also the fraction of premixed combustion is much stronger for conventional fuel (MK1) than for F-T fuels as shown by the evaluated rate of heat release in the premixed zone. This is an indication of smooth engine running, lower combustion rate, and lower NOx formation. As a complement to this, the cylinder pressure characteristic is more favourable when the engine runs on F-T fuel, with lower peak and earlier location.

As a conclusion of the experimental investigation on the single cylinder research engine it may be stated that F-T fuels can be used in unmodified compression ignition engines with significant reduction of regulated emission and smoother thermodynamic characteristics. Also substantial qualitative reductions, e.g. reduction of the number of hazardous chemicals and reduction of the concentration of hazardous chemicals in the exhausts has been realised. Further optimisation of parameters such as injection timing and its CAD position or F-T fuel composition might lead to still lower exhaust emissions.

It can be noted that both F-T fuels have very low densities, 744 and 761 kg/m^3 respectively. Several vehicle manufacturers have earlier stated that a fuel with a density below 800 kg/ m^3 would give functional problems with the engine. A minimum density of 800 kg/ m^3 is also required according to the European standard EN590 for diesel fuels. However, this seems to be a misunderstanding, based on the fact that low-density fuels have earlier often been based on jet kerosene, which has a very low cetane number. It can be surmised that it is actually the low cetane number which has given engine malfunction in earlier tests of low-density fuels, and not the density as such.

Despite a lower density, both F-T fuels have a higher energy content per litre than MK1 fuel. This is due to a high hydrogen-content in saturated non-cyclic compounds, such as those used in the F-T fuels. This is contrary to the common assumption in the vehicle industry that the energy content per litre of fuel is approximately proportional to the density.

ACHIEVING SUFFICIENT LUBRICITY

It is well-known in the trade that an important drawback of the paraffinic fuels described above is that they will not have sufficient lubricity in themselves, but an additive which improves lubricity must be employed. The limit for an acceptable fuel is usually given as HFRR wear scar, and this parameter must be below 400 micro-meters for an acceptable diesel fuel.

Initially, a commercial lubricity improving additive was used. It was found that this compound had a fully acceptable effect on the lubricity of the fuel, with values below 400 micro-meters in the HFRR wear scar test.

However, another option would be to use either a fat of biological origin or a methylated ester of a fat of biological origin as an additive. This would have the advantage of increasing the content of renewables in the fuel, thereby further decreasing emissions of greenhouse gases.

Adding a methylated ester of a biological fat to improve lubricity

An addition of 2.5% methylated ester of rape-seed oil (RME) in each of the two fuels F-T1 and F-T2 was found to give a fully acceptable effect on the lubricity of the two fuels, both fuels giving values under 400 micro-meters in the HFRR wear scar test.

The addition of RME to the fuels also gave surprising and unexpected positive effects on the colouring and smell of the fuel. RME has a clearly oily-olefinic smell, and a brown to yellow colouring, whereas paraffins are usually colourless and have a neutral to stale smell. However, the mixture, surprisingly, has a fresh but discrete lemony smell, and a slightly green colouring. These aesthetic effects are particularly attractive for an environmentally compatible fuel, and is therefore described here as one preferred embodiment of the present invention.

Adding a biological fat to improve lubricity

However, the methylation of rape-seed oil to RME is a costly process, and if rape-seed oil or other biological oils could be used directly, this would decrease the cost of the fuel, and also decrease both technical risks and the perceived health hazards of the fuel.

Rape-seed oil is an essentially poly-unsaturated vegetable oil, whereas olive oil is an essentially mono-unsaturated vegetable oil, and cocoanut oil is essentially a saturated vegetable oil. These three biological fats were therefore added, 2% each, to a FT fuel. Without additives, the FT fuel had a HFRR wear scar of 642 micro-meters, a viscosity of 2,73 mm^2/s, and a cold filter plugging point (CFPP) of -36°C.

It was found that the addition of 2% rape-seed oil to the FT fuel decreased the HFRR wear scar to 289 micro-meters. It would therefore give desired lubrication properties at this low percentage. The viscosity increased to 2,83, which is close to commercial high-aromatics diesels. A high viscosity is advantageous, since it will make injection of the fuel into the engine easier, and thereby contribute to a high efficiency in the combustion.

The CFPP decreased to -44°C, which is highly unexpected, since this is a value far below that of pure rape-seed oil and far below the -36°C of the FT fuel. The low CFPP is a highly attractive quality in arctic climates, where temperatures can reach -40°C or less.

The addition of 2% olive oil to the FT fuel also gave a very good lubricity value, 317 micrometer HFRR. Similarly to rape-seed oil, the viscosity increased somewhat, to 2,81, a value close to the viscosity of commercial high-aromatics diesels. Also here, the CFPP decreased to -44°C.

The addition of 2% cocoa-nut oil to the FT fuel also gave an acceptable lubricity value, 380 micro-meter HFRR. The viscosity increased to only 2,77, and the CFPP increased dramatically to -12°C.

The conclusion was that a few percent of a mono- or poly-unsaturated biological fat would improve lubricity greatly, while simultaneously increasing viscosity and decreasing CFPP. The use of fully saturated fats, such as cocoa-nut fat could not be recommended in arctic climates, and probably more that 2% should be added in order to achieve a stable and good lubricity in non-arctic climates.

A PROCESS FOR TAILORING AN ALTERNATIVE FUEL FOR A SPECIFIC MARKET

One possible method for designing an alternative fuel with low emissions and low toxicity for a specific market would then be to follow a four-step process:

1. Use C7+ n-paraffins as a base for the fuel
2. Adjust cold flow properties by addition of as much iso-paraffins as necessary
3. Adjust lubrication properties by adding as much biological fat or methylated ester of a biological fat as necessary
4. Add other minor additives as required in the specific market

Each of these steps will be described in more detail below.

Use n-paraffins as a base for the fuel

Before the fuel compositions were prepared, a combustion experiment was carried out in the following way:

A drop of a substance was introduced into a combustion chamber with a temperature between 500 and 800 degrees C. The exhausts from the chamber were analysed using a GC-MS instrument.

It was found that the exhausts from n-paraffins did not contain any cyclic substances, whereas some traces of cyclic substances were found when using iso-paraffins or alcohols. The conclusion was that n-paraffins would give the lowest possible content of cyclic substances in the exhaust.

Thus, the motivation for using n-paraffins as the base for an alternative fuel is the following:

(a) Pure n-paraffins will not give any cyclic substances when combusted. Thus, the emissions will be free from cyclic substances, which are often toxic, such as cyclohexane, benzene, polyaromatics, etc.

(b) n-paraffins have better lubrication properties than iso-paraffins, minimizing the need for lubrication additives.

(c) n-paraffins with more than 7 carbon atoms are essentially non-toxic. The chemical structure is similar to natural substances, such as natural fats. However, since the n-paraffin does not have the carboxylic group, the biological reactivity will be lower. In most mammals, n-paraffins will be broken down to non-toxic karboxylic acids. Karboxylic acids are used as energy storage in mammals.

(d) n-paraffins are very good fuels in compression engines, with high cetane number, and will thereby also give efficient and low-emission combustion. Hexadecane, or cetane, has a cetane number of 100 by definition, and other n-paraffins will also have high cetane numbers.

(e) n-paraffins are often less costly to manufacture than iso-paraffins.

However, since n-hexane (C_6H_{14}) is known to be toxic, it should be avoided as far as possible in any fuel formulation.

Adjust cold flow properties by addition of as much iso-paraffins as necessary

A purely n-paraffinic fuel containing a mixture of C7+ n-paraffins could have bad cold flow properties, leading to solids formation and plugs in the fuel system if the temperature dropped below a certain point. There are several possibilities of solving this problem:

(a) displace the spectrum of n-paraffins towards lighter n-paraffins, say C7-C10, which will lower the melting point of the fuel. However, this may lead to non-optimal use of the raw material, since C11+ n-paraffins then may need to be cracked to shorter paraffins. It also leads to competition for the raw material with jet fuel, since C7-C10 n-paraffins have an important market as jet fuel.

(b) add slightly branched iso-paraffins, some of which have a much lower melting point than n-paraffins with the same number of carbon atoms. The effect of branching on the melting point can be demonstrated by the following compounds: hexane (C_6H_{14}) melts at -95 degrees C, 2-methyl-pentane (C_6H_{14}) melts at -153,67 degrees C, whereas 3-methyl-pentane (C_6H_{14}) melts at -118 degrees C.

(c) add cold flow improvers. However, cold flow improvers mainly act as anti-crystallization compounds, and will thus fail to work at consistently low temperatures, such as arctic climates.

Thus, the preferred method would be to use as short C7+ n-paraffins as possible, and then add iso-paraffins with a low melting point as required to attain good cold flow properties.

<u>Adjust lubrication properties by adding as much biological fat or an ester of a biological fat as necessary</u>

Though n-paraffins usually have better lubrication properties than iso-paraffins, the lubrication properties are usually not sufficient for use in modern compression engines. The conventional method of attacking this problem is by addition of a commercial lubrication improving agent. However, the addition of a methylated ester of rape-seed oil was found to give a number of advantages over the conventional method:

(a) An addition of 2.5% RME to paraffinic fuel gave lubrication properties superior to MK1 diesel with synthetic lubrication improvers (HRRR wear scar 370 micrometers for MK1, versus HFRR wear scar 270 micrometers for paraffinic fuel with 2.5% RME)

(b) The fuel will have an increased renewable content

The addition of an unsaturated fat of biological origin had an even greater positive effect on the properties of the fuel:

(a) An addition of 2% olive oil or rape-seed oil gave lubrication properties superior to commercially available diesels

(b) The fuel will have an increased renewable content

(c) The viscosity increases to values close to commercial high-aromatics diesels, making it easier to achieve high efficiency in unmodified compression engines.

(d) The cold filter plugging point decreases, a clear advantage in arctic climates.

(e) The mixture of paraffinic fuel and in particular olive oil had an attractive greenish coloring and a discrete attractive smell.

(f) It is easier and cheaper to use a vegetable oil directly, instead of first converting the vegetable oil to a methyl ester of vegetable oil in a separate process.

Thus, in a preferred embodiment of the present invention, a fat of biological origin or a methylated ester of a fat of biological origin is added to the fuel, to attain the above attractive properties. Though only a few biological fats and methylated esters of biological fats were tested by us, it seems likely that other such fats and methylated and ethylated esters of such biological fats would give similar results.

Add other minor additives as required in the specific market

Other additives, such as bactericides and fungicides, may be needed, based on the market needs in the country in question. These additives are usually only added in a few ppm to the fuel, and will have a negligible effect on the overall combustion and lubrication properties of the fuel.

THE NEW LOW-EMISSIONS FUEL COMPOSITION

By using the process described, a fuel with the following components will be arrived at:

a) a main n-paraffinic component, constituting at least 60% of the total volume of the fuel,

b) an addition of up to 40 vol.-% iso-paraffins, in order to adjust cold-flow properties,

c) 0-20% linear-chain oxygenates, chosen to be miscible with the main n-paraffinic component, and with at least five carbon and oxygen atoms in the longest linear chain,

d) 0-20% lubricants chosen from the group consisting of fats of biological origin, and methylated esters of fats of biological origin.

e) optionally other minor additives, such as fungicides or bactericides, according to market needs.

Conclusions, Ramifications, and Scope of Invention

Accordingly it is evident that the utilization of catalytic carbon capture of the present invention will provide for a high energy efficiency and a high carbon capture ratio, thereby greatly decreasing net emissions of greenhouse gases to the atmosphere.

The economics of the process is much superior to earlier proposed processes, since competing plants for waxes, lubricants, and specialty fuels are not much bigger than a typical off-gas plant. By choosing the operational conditions of the reactor 24, the output can be adjusted to almost any size of plant, and any local markets for the end-products.

The compression engine fuels that can be produced according to the present invention have particularly attractive qualities, such as:

(a) High cetane number, typically 60-70 versus around 40 to 50 for standard diesel. A high cetane number gives an efficient combustion, and low emissions.

(b) Lower emissions and lower overall toxicity of all regulated and unregulated compounds compared to the main competing product, Swedish MK1 (also referred to as "city diesel"). To be noted especially is that the emissions are free from significant traces of heavy carcinogenic compounds, such as polyaromatics, even when the analysis is done using advanced GC-MS analysis equipment.

(c) The fuels can be used in standard compression engines, without any modifications needed, neither to the engine nor the fuel system.

(d) lower ignition delay and longer combustion duration than other commercial fuels, giving lower NOx emissions and an efficient combustion

(e) higher efficiency than the main competing product, Swedish MK1 diesel

(f) superior lubrication properties with an addition of a few percent of a vegetable oil, or an ester of a vegetable oil.

While the above description contains many specificities, these should not be construed as limitations on the scope of the invention, but rather as exemplifications of preferred embodiments thereof. Many other variations are possible.

Examples of variations of the process are that various off-gases may be used in the process, e.g.:

(a) off-gases from steel manufacturing: coking gas, blast furnace gas, or direct reduction gas

(b) off-gases from aluminum manufacturing from bauxite or other aluminum-bearing material

(c) off-gases from the production of sodium hydroxide and chlorine gas

(d) off-gases from acetylene manufacturing

Another set of variations include other catalytic processes in the catalytic reactor 24.

A third set of variations include that elements of the plant may switch places, e.g. carbon dioxide removal may in some cases be done before shift, or the off-gas holder 14 may be placed after the compression 16.

A fourth set of variations comprise elements that are omitted. For example, the shift reactor 18 may be omitted, if the carbon monoxide to hydrogen ratio is already adjusted to a ratio acceptable to the reactor 24. The off-gas holder 14 may be omitted if the flow of off-gas is continuous.

A fifth set of variations include that any of the industrial off-gases mentioned above may be mixed with other types of off-gases or waste gases from incineration.

A sixth set of limitations includes variations in the paraffinic composition of the fuel, as well as the use of other oxygenates as combustion improvers, and the use of other esters of triglycerides to achieve sufficient lubricity properties.

Accordingly, the scope of the invention should be determined not by the embodiment illustrated, but by the appended claims and their legal equivalents.

CLAIMS

1. A process for the catalytic carbon capture from carbon-bearing industrial off-gases comprising:

(a) collecting carbon-bearing off-gases

(b) compressing the gas to an elevated pressure

(c) having the gas passing a shift reaction

(d) having the gas passing a catalytic reaction to convert its content of carbon monoxide and hydrogen to give saturated non-cyclic hydrocarbons, non-saturated non-cyclic hydrocarbons, oxygenates and water.

2. A process according to claim 1, in which additional gas is generated and mixed with said off-gas before the mixture is passed on to said catalytic reactor.

3. A process according to claim 2, in which the process of generating said additional gas is selected from the group consisting of pyrolysis, partial oxidation, gasification, electrolysis, plasma excitation, water shift, inverse water shift, steam reforming, and catalytic reforming.

4. A process according to claim 1, in which said catalytic reactor is chosen from the group consisting of fischer-tropsch reactors, water shift reactors, and oxo synthesis reactors.

5. A process according to claim 1, in which said carbon-bearing substances are selected from the group consisting of alkanes, alkenes, alkynes, alcohols, ketones, organic acids, esters, and aldehydes.

6. A process according to claim 1, in which said carbon-bearing substances have applications selected from the group consisting of heating fuel, candle wax, lamp fuel, engine fuel, and turbine fuel.

7. A process according to claim 6, in which said carbon-bearing substances are subsequently stabilized by hydrogenation.

8. A process according to claim 1, in which the source of said off-gas is selected from the group consisting of steel manufacturing, aluminum manufacturing, and acetylene gas manufacturing.

9. A process according to claim 1, in which said carbon-bearing substances are subsequently stabililized by hydrogenation.

10. A process for catalytic carbon capture using hydrogen-bearing off-gases consisting of

(a) mixing said hydrogen-bearing off-gas with a carbon-bearing off-gas, forming a synthesis gas,

(b) passing said synthesis gas on to a catalysis reactor, in which chemical reactions of said synthesis gas takes place, said catalysis reactor being chosen from the group consisting of Fischer-Tropsch reactors, water shift reactors, and inverse water shift reactors.

(c) a vessel for collecting carbon-bearing substances, whereby a decrease in net emissions of carbon-bearing gases to the atmosphere can be effected.

11. A process according to claim 10, in which said carbon-bearing substances are selected from the group consisting of alkanes, alkenes, alkynes, alcohols, ketones, organic acids, esters, and aldehydes.

12. A process according to claim 11, in which said carbon-bearing substances are subsequently stabilized using hydrogen gas and a catalyst.

13. A process according to claim 10, in which said carbon-bearing substances have applications selected from the group consisting of heating fuel, candle wax, lamp fuel, engine fuel, and turbine fuel.

14. A process according to claim 13, in which said carbon-bearing substances are subsequently stabilized using hydrogen gas and a catalyst.

15. A process according to claim 10, in which said carbon-bearing gas is generated by a process selected from the group consisting of incineration, pyrolysis, partial oxidation, gasification, water shift, inverse water shift, steam reforming, and catalytic reforming.

16. A process according to claim 15, in which said carbon-bearing substances are subsequently stabilized using hydrogen gas and a catalyst.

17. A fuel, which besides common additives, comprises at least 70% per volume of iso- and n-paraffins,

18. A fuel according to claim 17, which comprises

(a) approximately 60.0-99.99 Vol.-% n-paraffins, said n-paraffins having a boiling point of beetween 150 and 360°C,

(b) approximately 0.001-40.0 Vol.-% iso-paraffins, said iso-paraffins having a boiling point of between 150 and 360°C

19. A fuel according to claim 17, which comprises

(a) approximately 60.0-99.99 vol.-% n-paraffins, said n-paraffins having a boiling point of between 150 and 360°C

(b) approximately 0.001-40.0 vol.-% iso-paraffins, said iso-paraffins having a boiling point of between 150 and 360°C

(c) approximately 0.001-20.0 vol.-% of a substance chosen from the group consisting of fats of biological origin, methylated esters of said fats, and ethylated esters of said fats

20. A fuel according to claim 19, in which said fat of biological origin is an oil from a plant selected from the group consisting of rape, corn, sunflower, olive, peanut, flax, cocoa, hemp, and soya bean.

21. A fuel according to claim 17, in which said non-cyclic paraffins have been manufactured using Fischer-Tropsch synthesis from raw materials selected from the group consisting of industrial off-gases, waste, wood chips, sewage sludge, and renewable raw materials.

22. A fuel according to claim 17, wherein the fuel has a content of aromatic components lower than 2 % per volume.

23. A fuel according to claim 22, wherein the fuel has a sulphur content lower than 5 mg per kg.

24. A fuel according to claim 23, wherein the fuel has a content of polyaromatic compounds lower than 0.02 % per volume.

25. A fuel according to claim 24, wherein the fuel has a density lower than 800 kg per cubic metre.

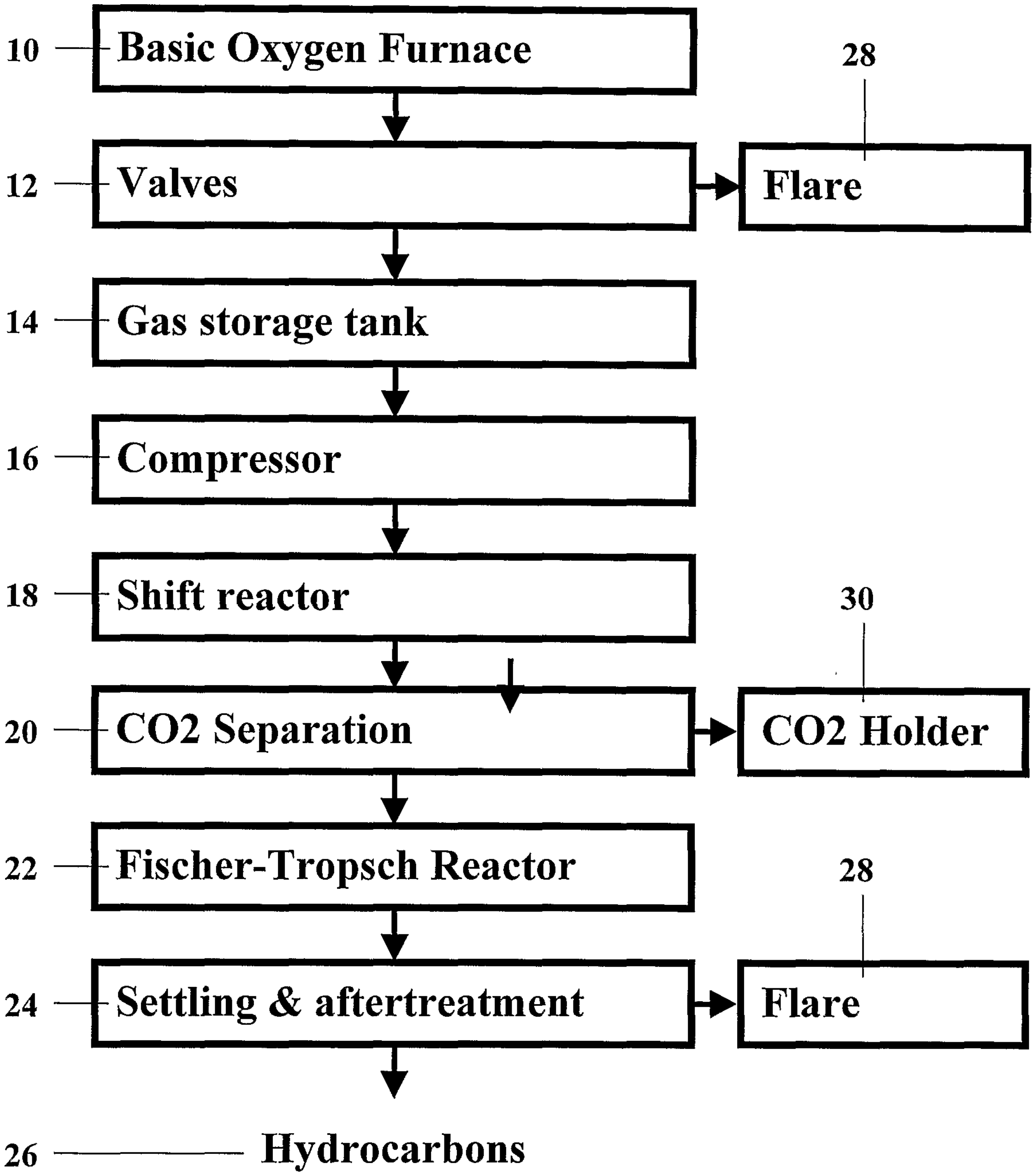

Fig. 1. Process flow for basic oxygen furnace gas

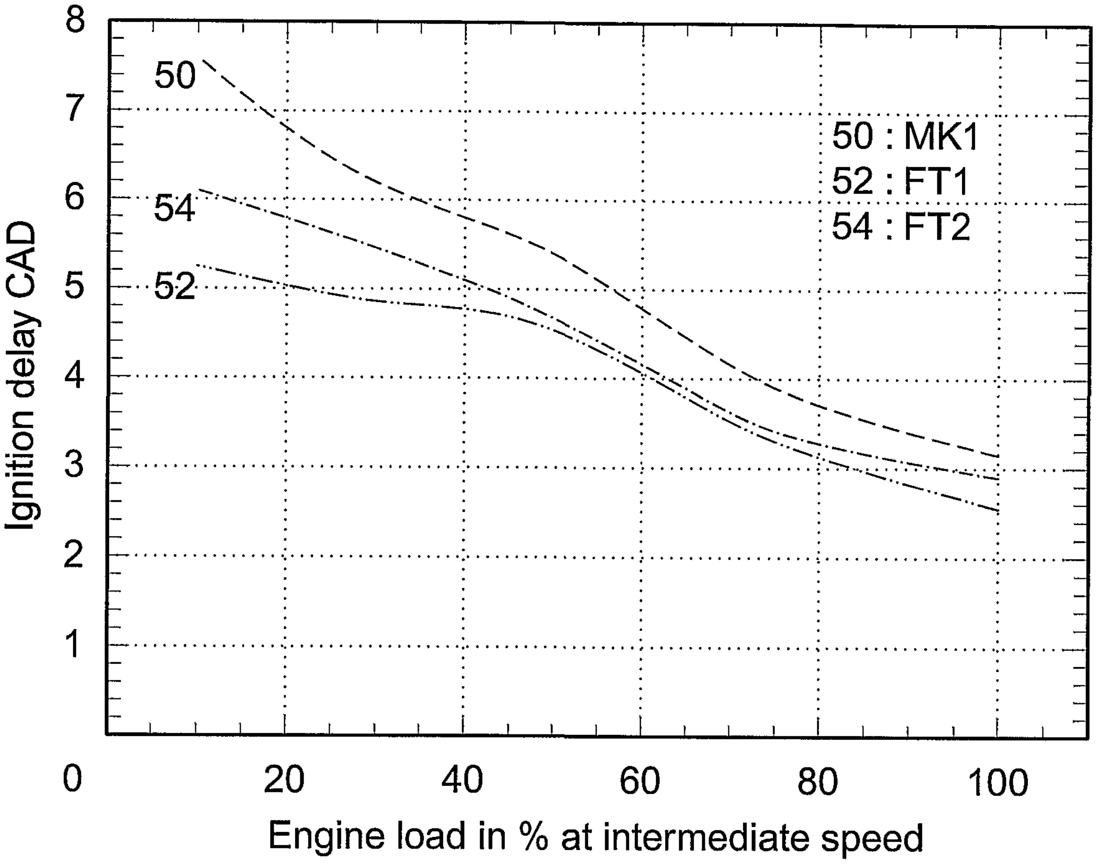

Figure 2. Ignition delay in CAD as a function of engine load