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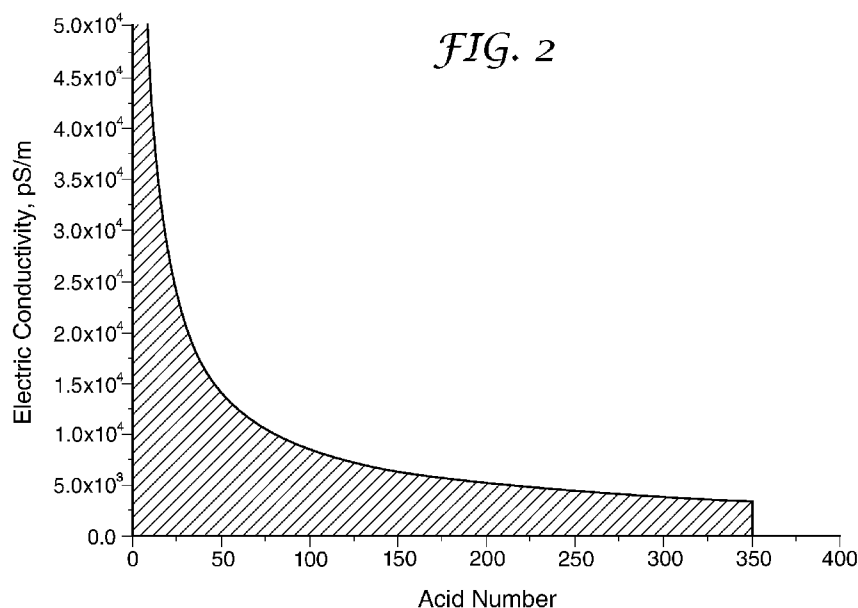
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(54) Title: RENEWABLE FUEL



(57) Abstract: A method for determining the suitability of an acid oil or fat as a renewable fuel for combustion in a compression ignition engine, the method comprising: (a) measuring the electrical conductivity (EC) value at 60°C and acid number (AN) value of a sample of the acid oil or fat; (b) determining whether the values fall in the hatched region in Figure 2; and (c) if the values fall in the hatched region, determining that the acid oil or fat is suitable for combustion in a compression ignition engine.

RENEWABLE FUEL

BACKGROUND

5 a. Field of the Invention

The present invention relates to a method of determining the suitability of an acid oil or fat for combustion in a compression ignition engine. Other aspects provide a novel renewable fuel, and an apparatus and method for the preparation of such a
10 fuel.

b. Related Art

Naturally occurring renewable oils and fats are extracted from plants or rendered
15 from animals in distinction from fossil fuels. There are over forty different fatty acids that can combine with glycerine to form a variety of naturally occurring oils and fats, including oils and fats derived from seeds, such as rape, sunflower and ground nut, or fruit, such as palm or coconut, as well as oils and fats derived from fish or animals. Typically the term "oil" is used for substances in a liquid state at
20 ambient temperatures, whereas fats tend to be solid or semi-solid at room temperatures.

Oils and fats that contain free fatty acids are commonly known as acid oils or fatty acid oils. The term "acid oil" can refer to various oils and fats and for clarity
25 includes crude oil derived from seeds, fruit, fish or animals. Such oil will normally contain significant amounts of free fatty acids as well as other contaminants. The crude oil may be oil that has been simply pressed from seeds or fruit, or may be a blend of pressed oil and soil extracted oil. Acid fat is acid oil that is in a solid or semi-solid state at normal ambient temperature and crude acid fat is also derived
30 from seeds, fruit, fish or animals. The term "acid oil" will be used herein to include acid fats unless the context otherwise dictates.

Acid oils and fats are characterised by different parameters related to the physical

and chemical properties of the substance. In particular, a number of parameters are used to define the suitability of the material to be used as the fuel in internal combustion engines. Among these parameters are the acid number and the iodine number. The acid number is used to quantify the amount of acid present in biodiesel, and in particular is a measure of the amount of carboxylic acid groups in a fatty acid. The acid number is defined as the mass of potassium hydroxide (base) in milligrams needed to neutralise the acid groups in one gram of biodiesel.

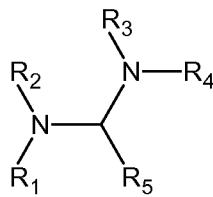
It is known that the acidity of fuel is important, as highly acidic fuels can cause corrosion of engine components such as fuel injectors , injection pumps and seals. Therefore, there are a number of standards that specify the maximum limit of the acid number of biodiesel. For example EN 14214 specifies the maximum acid number as 0.5 mg KOH/g.

However, a number of engine manufacturers and suppliers have set higher limits than those specified by the standards. For example, Wartsila stipulates a maximum acid number of 5,0 mg KOH/g and a maximum iodine number of 120 for the renewable fuels for its diesel engines. Similarly, MAN Diesel stipulates a Total Acid Number (TAN) of less than 4 mg KOH/g and an iodine number less than 125 g/100g for its biofuel.

These restrictions on the acidity of the fuel preclude the use of neat acid oil and fats as fuels for internal combustion engines as their acid numbers are significantly higher than the specified maximum. However, these materials possess quite high calorific value and are a potentially valuable renewable fuel.

US patent 4,978,366 teaches the use of distillate fuels which have a high acid number initially or which develop a high acid number as a result of fuel degradation by stabilizing them with diaminoalkanes with the formula

- 3 -



where R₁-R₅ are different hydrocarbon substituents. A disadvantage of this method is that it is limited to distillate fuels with relatively low acid number 2 or 3, albeit
5 higher than those specified in the standards. For fuels with a very high acid number a large amount of the additive would be required, rendering the method impractical.

Therefore, there is a need to provide an apparatus or method to enable fuels with
10 a high acid number to be used in internal combustion engines.

SUMMARY OF THE INVENTION

Aspects of the invention are specified in the independent claims. Preferred
15 features are specified in the dependent claims.

The invention provides stable combustion of acid oils without any detrimental corrosion of standard diesel engine fuel injection equipment or significant deposit formation on the injector nozzle tip.

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The renewable compression ignition engine fuel from acid oils and fats is of particular applicability for combined heat and power (CHP) plants.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be further described by way of example only, with reference to the following drawings, in which:

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Figure 1 shows acid and iodine numbers of conventional diesel fuels and acid oils suitable for use in an embodiment of the invention;

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Figure 2 shows the acceptable region of electrical conductivity values measured at 60°C and acid numbers for the renewable acid oils and fats in accordance with aspect of the invention;

15

Figure 3 shows apparatus for the treatment of acid oils and fats according to a preferred embodiment of the invention;

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Figure 4 shows the nozzle deposits of a compression ignition engine fuel injector after 1.5 hours running on an acid oil prepared according to the present invention;

Figure 5 shows the nozzle deposits of a compression ignition engine fuel injector pump after 1.5 hours running on simply cleaned acid oil;

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Figure 6 shows a compression ignition engine fuel pump after 1.5 hours running on an acid oil prepared according to the present invention;

Figure 7 shows a compression ignition engine fuel pump after 1.5 hours running on simply cleaned acid oil;

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Figure 8 shows a fuel injection needle of a compression ignition engine after 1.5 hours running on an acid oil prepared according to the present invention; and

Figure 9 shows a fuel injection needle of a compression ignition engine after 1.5 hours running on simply cleaned acid oil.

DETAILED DESCRIPTION

The shaded rectangular region of Figure 1 indicates the accepted range of acid numbers and iodine numbers of fuels that may be used in compression ignition engines. As can be seen, this region includes a number of fuel specifications currently in use in different countries, including those adopted by MAN and Wartsila. Those fuels lying in the shaded region but having acid numbers greater than 0.5 generally require some modifications to be made to the engine before they can be used. These modifications may include, for example, replacement seals and injection equipment materials.

Naturally-derived oils and fats typically have acid numbers between about 10 and 500, for example tallow, rapeseed oil distillate and palm fatty acid distillate (PFAD). Currently, these oils are unsuitable for use in standard engines, even with modifications, due to their high acidity. Therefore, currently these acid oils must be treated to reduce the level of fatty acids to an acceptable amount.

We have surprisingly found that if the electrical conductivity (EC) of an acid oil or fat is of a suitable value, then significantly higher acid number (AN) materials may be combusted without deleterious effects on the combustion apparatus. In particular, we have found that if the EC value falls on the curve of Fig. 2 or below it (in the hatched area) then this acid oil or fat is suitable for use as fuel for a compression ignition engine. We have further developed a method and an apparatus for decreasing the electrical conductivity of acid oils and fats to render them suitable as renewable fuels for the compression ignition engine.

In contrast to the prior art, the apparatus and method of aspects of the present invention renders these acid oils and fats suitable for direct feeding to a compression ignition engine, without reducing their acid numbers. We have surprisingly found that decreasing the conductivity of crude acid oil drastically reduces its corrosive properties and the resultant acid oil can then be combusted in an engine with little or no modification. This could be achieved by removing highly-conducting impurities and impurities with a high dielectric constant, for

example by centrifuging the acid oil and then (optionally) passing it through an evaporator.

We have established the experimental dependence between the fuel acid number (AN) measured according to ASTM D974 (ASTM D664) as mg KOH needed for neutralisation of 1 g of oil and maximum allowable electrical conductivity level below which no corrosion of injection equipment or engine cylinders occurs.

Figure 2 shows this dependence. If values of EC (pS/m) of the acid oil measured at 60°C lie on the curve or fall below it (in the hatched region) then the acid oil could be used in the engine without any danger of inflicting corrosive damage onto the injection equipment or cylinders. Thus, the hatched area of Figure 2 defines the safe operating region. The hatched area is defined by Equation 1:

$$EC(pS/m) = \left(4.85 \cdot 10^{-8} + 5.0 \cdot 10^{-8} \times AN\right)^{-1/1.35} \quad \text{- Equation 1}$$

Where AN is mg KOH/g oil.

Figure 3 shows a schematic of an embodiment of apparatus for the treatment of acid oils according to an embodiment of the present invention. The acid oil to be treated is stored in a tank 1. The acid oil then flows or is pumped into a centrifuge 2.

The centrifugation process is primarily used to remove conductive impurities and impurities with high dielectric constant like glycerine ($\epsilon \cong 47$) from the acid oil. Glycerine is an undesirable component of fuel as it causes injector deposits and may adversely affect cold weather operation of compression ignition engines. Because of the fluid density difference between the acid oil and glycerine, any free glycerine is quickly separated from the remaining acid oil. The heavy glycerine residue can then be removed.

To aid in this removal process, the centrifuge 2 is typically heated to a temperature

between 35 and 100°C. This reduces the viscosity of the acid oil making the separation of the glycerine more efficient. The raised temperature may also cause the loss of some water from the acid oil by evaporation.

- 5 In general, to obtain a high purity product with negligible remaining free glycerine, the oil has to be passed through a centrifuge a number of times. In this process however, the acid oil passes once through the centrifuge 2 to remove the majority of the glycerine and the resultant acid oil supernatant is then (optionally) transferred into an evaporator 3. The electrical conductivity of the resultant stream
- 10 is measured using the conductivity meter 5 that could be an in-line device or any electrical conductivity meter suitable for measuring the conductivity of low-conductive fluids.

- If the electrical conductivity of the resultant stream falls outside the crosshatched
- 15 region then the valve 6 is closed, valve 7 is opened and the acid oil is recirculated for the reprocessing.

- The evaporator 3 is used to remove any remaining conductive impurities or impurities with the high dielectric constant (for example, water ($\epsilon \cong 80$) and free
- 20 glycerine), from the acid oil.

- The evaporator 3 has a heat exchange surface held at an elevated temperature onto which the acid oil flows. The heat exchange surface typically includes the hot walls of the evaporator. The temperature of the evaporator 3 is typically in the
- 25 range 45 to 200°C, and is more preferably between 70 and 130°C. These temperatures accelerate evaporation of water from the acid oil. In addition, the evaporator 3 comprises a vacuum pump for generating reduced pressure in the evaporating chamber 3. This facilitates the removal of the higher boiling point glycerine without requiring higher temperatures. The reduced pressure is generally
- 30 in the range 0.5 to 250 millibar (50-2500 Pa). Preferably the reduced pressure is less than 5 millibar (500 Pa). As the acid oil is discharged into the evaporator 3 under this reduced pressure, the oil is forced out into a thin film over the hot surface.

The reduced operating pressure of the evaporator 3 causes the boiling points of the contaminants to decrease. Therefore, higher boiling point contaminants such as polyols, and in particular glycerol, that would otherwise have too high a boiling point under normal or ambient pressure, are vapourised when they come into contact with the hot surface of the heat exchanger. Furthermore, because the acid oil is spread into a thin film, a large amount of the oil is in contact with or in close proximity to the hot surface of the heat exchanger. In a preferred embodiment of the invention, the evaporator 3 is a thin-film evaporator. More preferably the evaporator 3 is a wiped-film evaporator in which the thin film of acid oil is created by wiper blades that move over the surface of the heated walls of the evaporator 3. The wipers pump the liquid through the chamber of the evaporator 3 and are particularly advantageous when processing more viscous oils.

15 The contaminant vapours that are formed then pass to a condenser (not shown). The vapours condense on the cold surfaces within the condenser and the resultant liquid is removed. The condenser may be external to the evaporator 3 or more preferably the condenser is an internal condenser. In this case, the evaporator 3 may be a short-path evaporator. This has the advantage that higher vacuums may be achieved in the evaporator 3, further lowering the boiling point of contaminants.

In order to remove as much glycerine and water as possible from the acid oil, the oil may be passed through the evaporator 3 a number of times. Preferably, the acid oil is cycled through the evaporator 3 until no more distillate is collected. As the residence time of the acid oil in the evaporator 3 is very short, and may only be a few seconds, the additional time taken to make multiple passes does not add significantly to the overall time taken to dry the acid oil and remove conductive contaminants like glycerine or water. When no further evolution of distillate is observed, the treated oil is deemed substantially free of conductive contaminants.

Once the acid oil leaves the evaporator 3 it is substantially free of both water and glycerine. The removal of these substances significantly decreases the

conductivity of the acid oil and in general the conductivity of the dried acid oil is less than half that of the crude oil. For example, the electrical conductivity of crude palm fatty acid oil distillate was measured to be 4700 pS/m at 60 °C, and this dropped to 1560-1630 pS/m following the drying process. Likewise, the conductivity of crude tallow was measured to be 15400 pS/m at 60 °C, while the conductivity of dried tallow was only 5800-6700 pS/m. Preferably the treated fuel has a conductivity less than half the value for the crude acid oil, preferably less than 45%, notably less than 35%.

- 10 The apparatus described above provides a means for producing a renewable fuel from acid oils and fats previously deemed unsuitable for combustion in a compression ignition engine 4 due to their high acid and iodine numbers. This is achieved by a reduction in the electrical conductivity of the oil by the removal of unwanted water and glycerine, which would otherwise be detrimental to the operation of the engine 4.

It has been found that it is the combination of high acid number and high conductivity of acid oil that renders it unsuitable for combustion in a compression ignition engine, and that by reducing the conductivity of the acid oil, it is then possible to combust high acid number oils in a standard diesel engine.

The method described above, therefore, does not decrease the acid number of the oil but only decreases its electrical conductivity by removing high-conductive contaminants and contaminants with the high dielectric constant. Further, the additional removal of glycerine not only prevents the build-up of deposits in the engine, but also further decreases the conductivity of the acid oil, as pure glycerine has a relatively high conductivity of between 4000 and 5000 $\mu\text{S/cm}$.

Treating high acid number acid oils to reduce their conductivity therefore allows them to be fed directly into a compression ignition engine. This method will now be further illustrated by the following example.

Example

Palm fatty acid oil distillate (PFAD) with acid number 298 and iodine number 57 was centrifuged using an SA-1 Westfalia centrifuge to remove particulate debris and free glycerine. The supernatant oil was then passed several times through a rotary evaporator at 90 °C and 2 millibar (200 Pa) residual pressure until no evolution of distillate was observed. The treated acid oil was then combusted in a Lister-Petter four cylinder direct injection compression ignition engine at constant power and speed (typical power generation conditions).

Combustion was initially carried out with gas oil, followed by comparative tests using PFAD treated according to the current invention and conventionally cleaned PFAD.

These results show that stable combustion of the acid oil treated according to the present invention was possible. The results are comparable and similar to those from the combustion of conventionally cleaned acid oil.

Furthermore, the combustion of the acid oils treated by centrifuging and evaporation processes showed no detrimental corrosion of standard diesel engine fuel injection equipment even though the acid number of the acid oil was not reduced. In addition, the removal of the free glycerine prevented any significant deposit formation on engine components.

Table 1: Results from combustion of conventionally cleaned PFAD

Exhaust Temp (°C)	Engine Speed (RPM)	Power (kW)	NOX (ppm)	CO (ppm)	Exhaust (O ₂ %)	Time since first run (mins)	Inlet Manifold Pressure (bar)
358	2353	16.41	821	146	12.36	0	1.53
352	2353	16.38	816	139	12.68	7	1.6
347	2362	16.33	792	155	12.71	18	1.59
348	2374	16.33	786	178	12.72	26	1.62
350	2331	16.19	793	198	12.62	32	1.59
350	2337	16.11	789	209	12.67	39	1.59
350	2333	16.01	768	225	12.65	44	1.6
351	2363	16.15	755	248	12.69	52	1.61
352	2359	16.13	743	254	12.64	62	1.62
354	2360	16.15	734	278	12.66	72	1.62
358	2298	16.16	778	262	12.38	82	1.59

Table 2: Results from combustion of PFAD treated according to the current invention

5

Exhaust Temp (°C)	Engine Speed (RPM)	Power (kW)	NOX (ppm)	CO (ppm)	Exhaust (O ₂ %)	Time since first run (mins)	Inlet Manifold Pressure (bar)
332	2328	16.36	778	118	13.03	0	1.6
336	2351	16.42	768	120	13.06	5	1.62
340	2302	16.41	829	114	12.81	11	1.6
346	2302	16.48	857	119	12.65	21	1.59
346	2301	16.42	860	118	12.63	29	1.59
346	2324	16.41	832	127	12.73	34	1.6
345	2342	16.46	819	123	12.71	41	1.62
346	2336	16.35	809	136	12.75	47	1.62
346	2333	16.19	796	149	12.73	52	1.6
347	2319	16.06	793	155	12.59	58	1.6
348	2336	16.21	772	154	12.38	66	1.62
348	2343	16.38	772	146	12.25	72	1.62
349	2343	16.36	779	134	12.11	79	1.61

As can be seen in Figure 5, following 1.5 hours running on conventionally cleaned acid oil significant deposits built up on the nozzle of the fuel injector. However, no

10

deposits were seen on a nozzle taken from an engine that had been running on acid oil treated according to the present invention, as shown in Figure 4.

Furthermore, as shown in Figures 6 and 7, corrosion was also noticeable on the injector needle seat area following combustion of conventionally cleaned acid oil, but significantly less corrosion occurred using the acid oil treated according to the invention.

Conventionally treated acid oil also caused significant corrosion of the fuel injection pump high pressure plunger (Figure 9) with only 1.5 hours running, due to the acidity of the oil. However, as seen in Figure 8, a reduction in the conductivity of the acid oil eliminated the corrosion even though the acid number of the oil had not been reduced during the treatment.

Further test results are summarised in Table 3.

Table 3 – Fuel Treatment Results

Fuel	Acid Number, mg KOH/g	Conductivity pS/m before treatment	Suitable for compression ignition engine and fuel systems?	Conductivity, pS/m post-treatment	Suitable for compression ignition engine and fuel systems?
Fuel 1 (fatty acids)	124	15,000	No	5,760	Yes
Fuel 2 (fats)	12	➤ Metering range	No	2,580	Yes
Fuel 3 (fats)	7	➤ Metering range	No	73,000	Yes
Fuel 4 (blend of fats & fatty acids)	26	140,000	No	65,400	Yes

CLAIMS

1. A method for determining the suitability of an acid oil or fat as a renewable fuel for combustion in a compression ignition engine, the method comprising:
- 5 (a) measuring the electrical conductivity (EC) value at 60°C and acid number (AN) value of a sample of the acid oil or fat;
- (b) determining whether the values fall in the hatched region in Figure 2 and
- (c) if the values fall in the hatched region, determining that the acid oil or fat is suitable for combustion in a compression ignition engine.
- 10
2. A method for the preparation of a renewable compression ignition fuel, the method comprising:
- reducing the electrical conductivity of the said fuel so it falls in the cross-hatched region shown in Figure 2.
- 15
3. A method as claimed in claim 2 where the electrical conductivity of the said fuel is reduced by centrifuging it to remove conductive impurities and impurities with a high dielectric constant.
- 20
4. A method as claimed in claim 2 wherein the fuel is an acid oil and wherein the electrical conductivity is reduced by:
- centrifuging the acid oil to remove conductive impurities and impurities with a high dielectric constant; and
 - passing the centrifuged acid oil through an evaporator to remove
- 25 conductive impurities and impurities with a high dielectric constant unseparable by centrifugation to produce a compression ignition fuel.
5. A method as claimed in claim 3, wherein the centrifuge is heated to between 35 and 100 °C.
- 30
6. A method as claimed in claim 4, wherein the evaporation is carried out under a pressure of between 0.5 and 250 millibar.

7. A method as claimed in any of claims 4-6, wherein the evaporator is heated to between 45 and 200 °C.

8. A method as claimed in any of claims 4-7, wherein the crude acid oil has an acid number of between 10 and 500.

9 A method as claimed in any of claims 4-8, wherein the evaporation is carried out until substantially no further distillate is produced.

10 10. A method as claimed in any of claims 2-9, further comprising the step of injecting the compression ignition fuel into the combustion chamber of a compression ignition engine and combusting the treated fuel under diesel-cycle conditions.

15 11. Apparatus for use in the method of claim 3, comprising:
- a centrifuge for removing conductive impurities from a crude acid oil; and
- an evaporator for receiving centrifuged acid oil from the centrifuge and evaporating low-boiling conductive impurities from the centrifuged oil;
- an electrical conductivity meter for measuring the conductivity of the
20 resultant acid oil.

12. Apparatus as claimed in Claim 11, further comprising a vacuum pump for generating reduced pressure in an evaporating chamber of the evaporator.

25 13. Apparatus as claimed in Claim 12, wherein the vacuum pump is capable of generating a pressure in the evaporating chamber of less than 5 millibar.

14. Apparatus as claimed in any of claims 11-13, wherein the evaporator is a rotary evaporator.

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15. Apparatus as claimed in any of claims 11-14, wherein the evaporator is a thin-film evaporator.

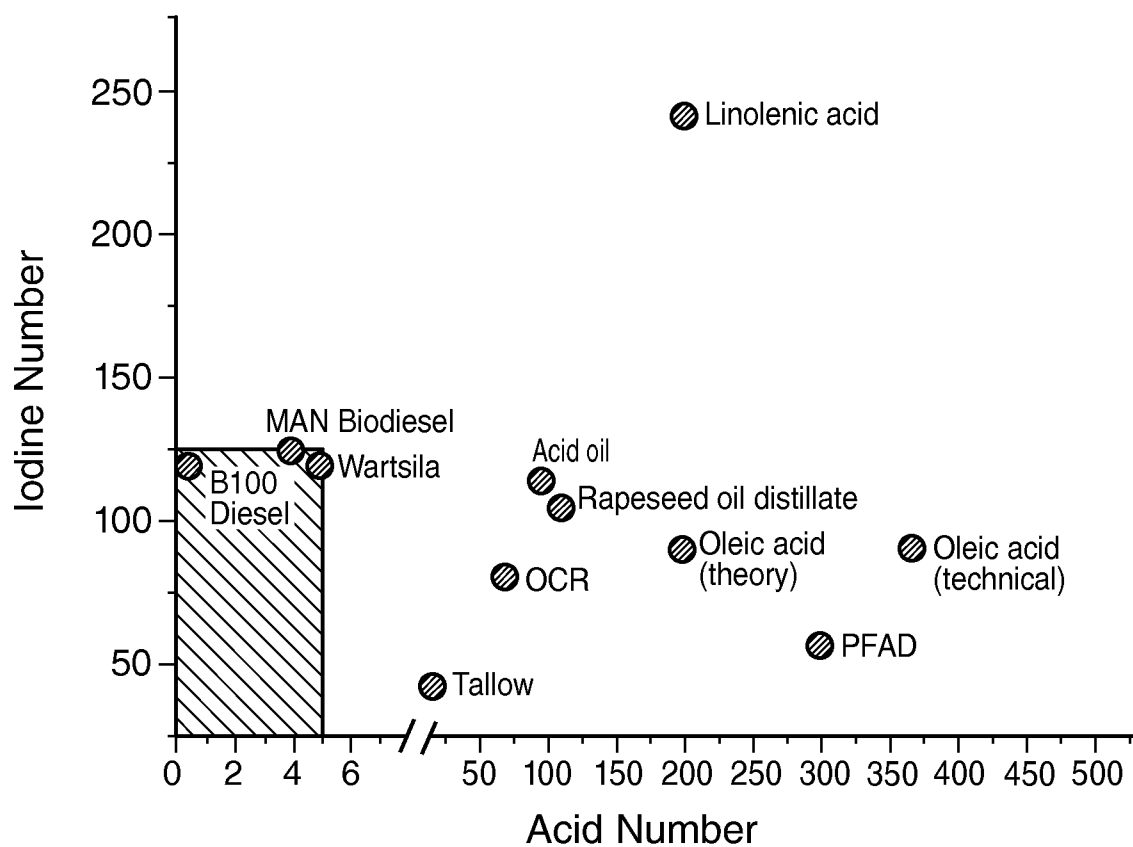
16. Apparatus as claimed in Claim 15, wherein the thin-film evaporator is a wiped-film evaporator.

17 Apparatus as claimed in any of claims 11-16, wherein the evaporator is a
5 short-path evaporator.

18 An engine assembly for combusting acid oils, the assembly comprising:

- a fuel tank for storing crude acid oil;
 - a centrifuge for receiving crude acid oil from the fuel tank;
 - 10 - an evaporator for receiving centrifuged acid oil from the centrifuge and removing conductive impurities by evaporation; and
 - a compression ignition engine, for receiving and combusting treated fuel from the evaporator.
- 15 19. A renewable compression ignition fuel comprising free fatty acids with a total acid number from 10 to 500 and with electrical conductivity values measured at 60°C falling substantially on the curve in the Figure 2 or below it.

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*FIG. 1* (PRIOR ART)

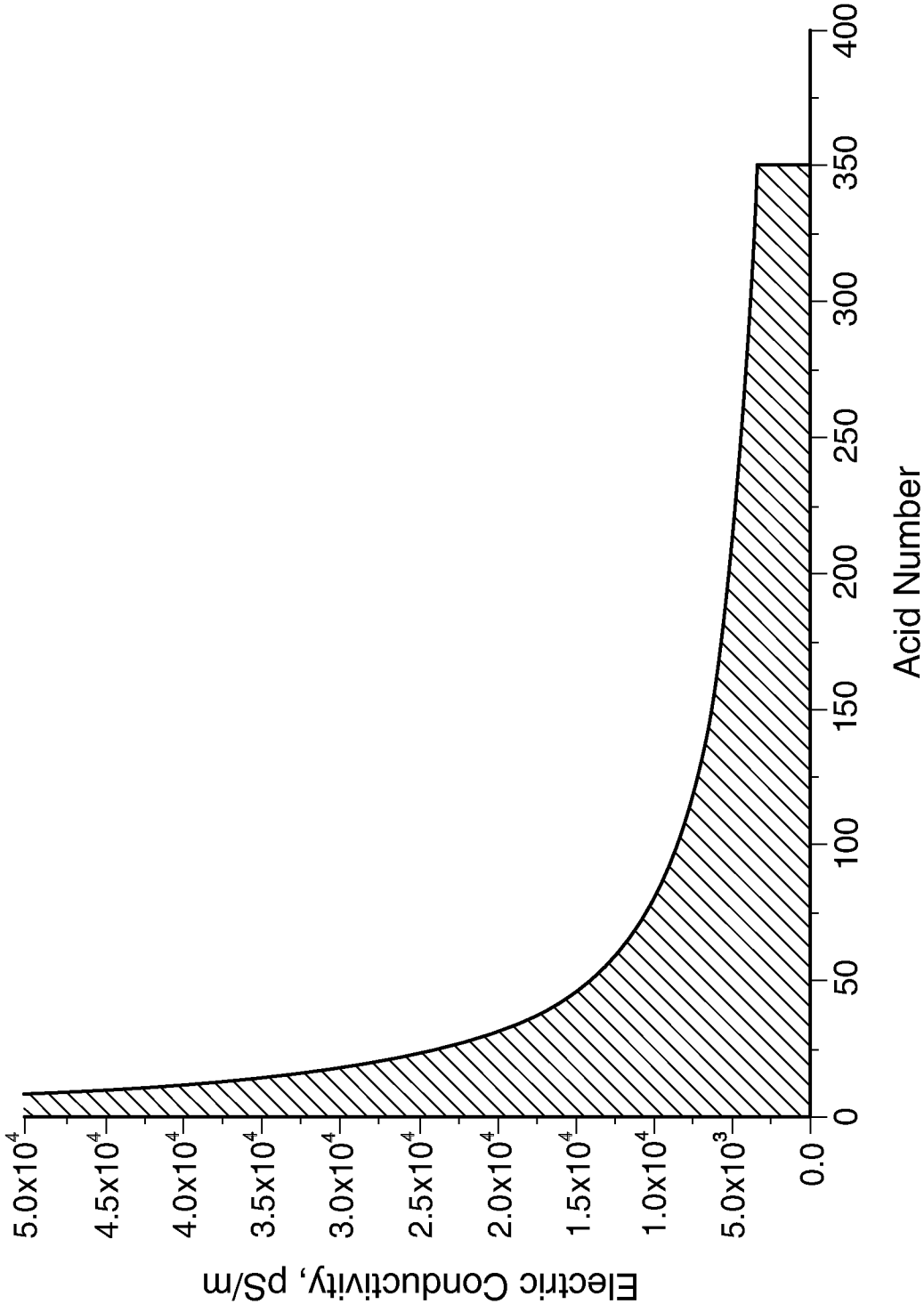


FIG. 2

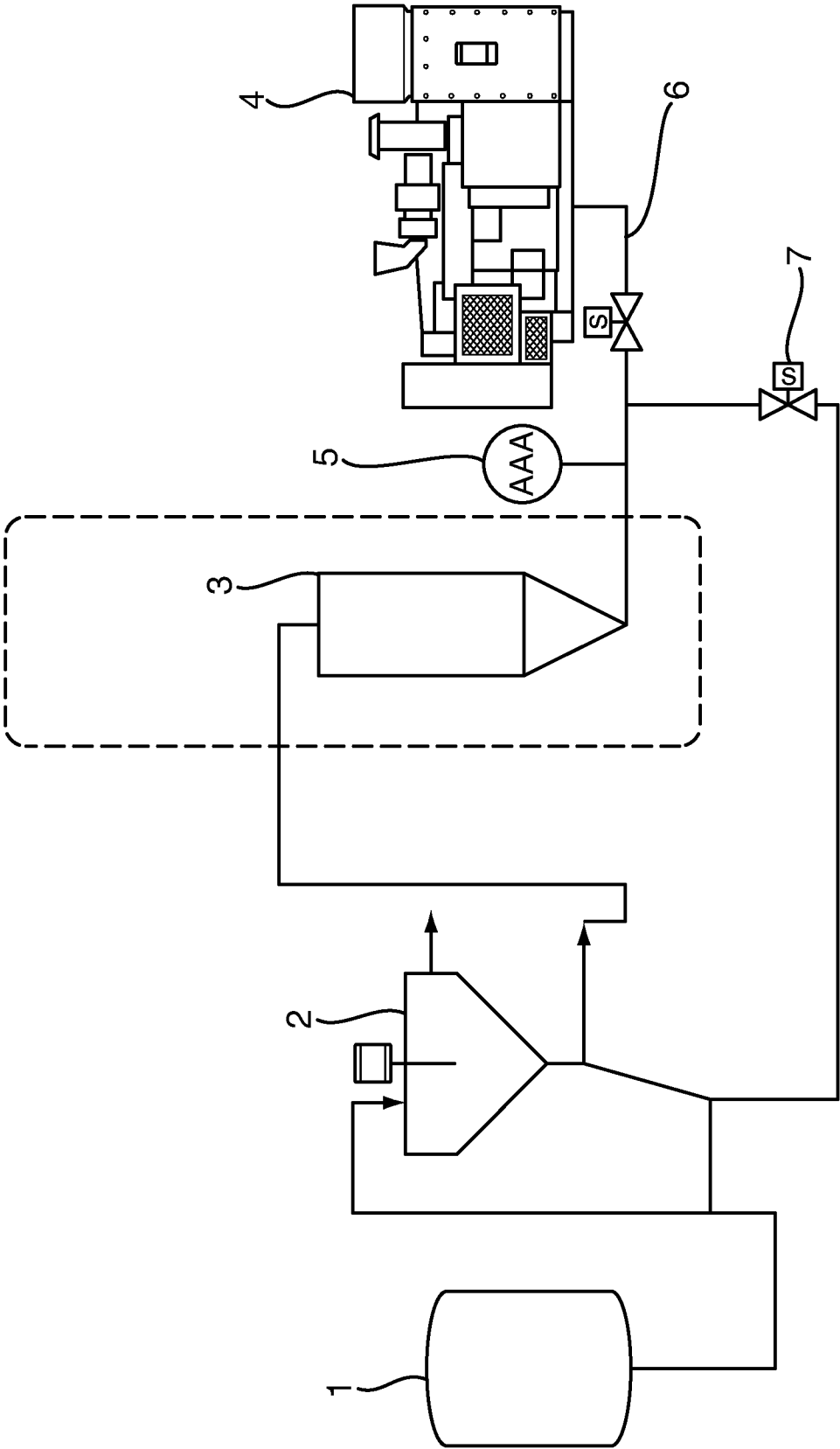


FIG. 3

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FIG. 4

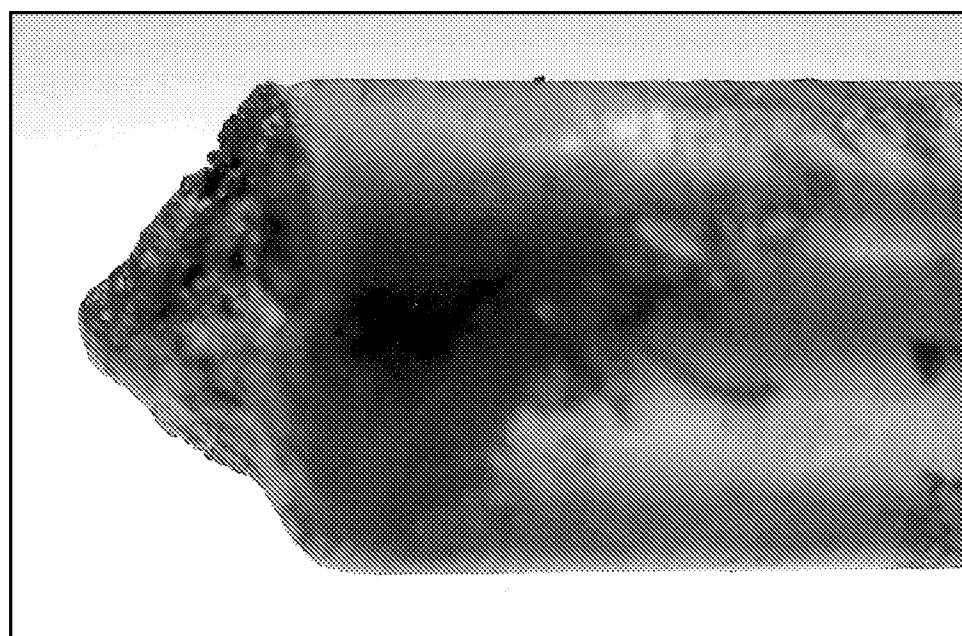


FIG. 5 (PRIOR ART)

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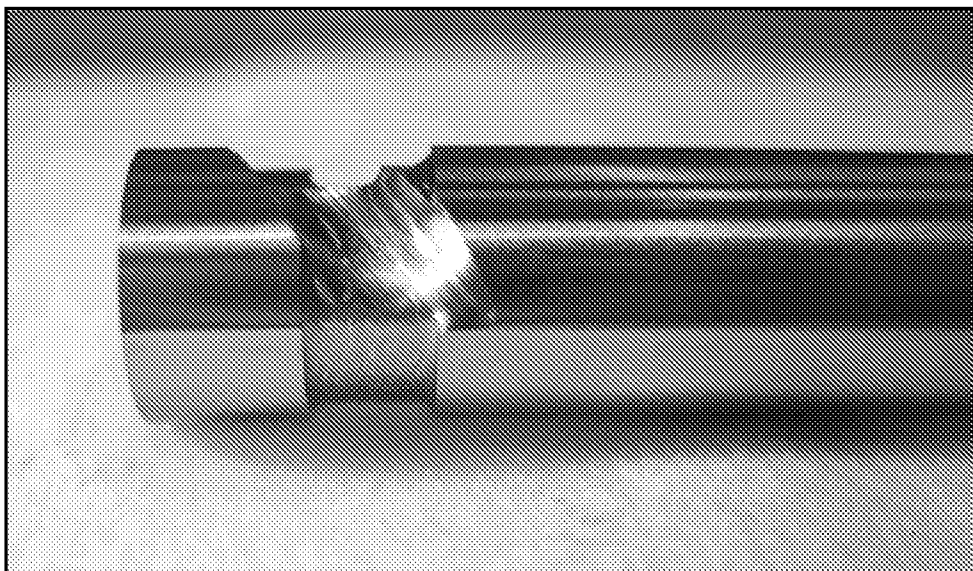


FIG. 6

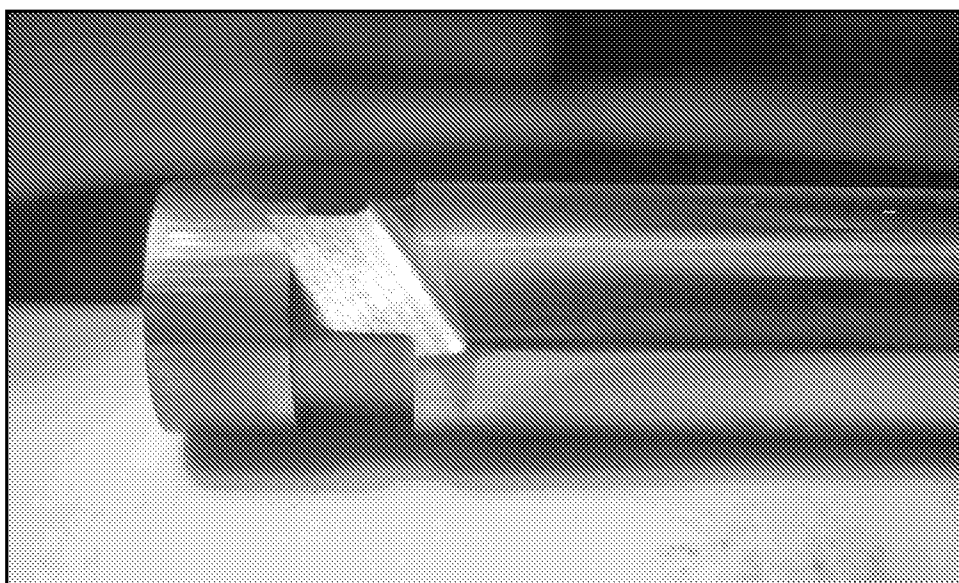


FIG. 7 (PRIOR ART)

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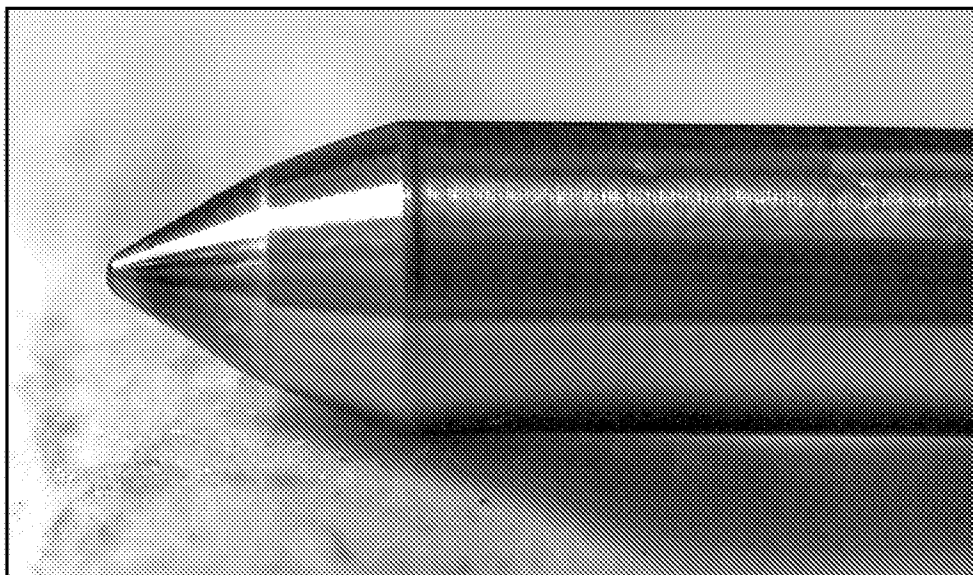


FIG. 8

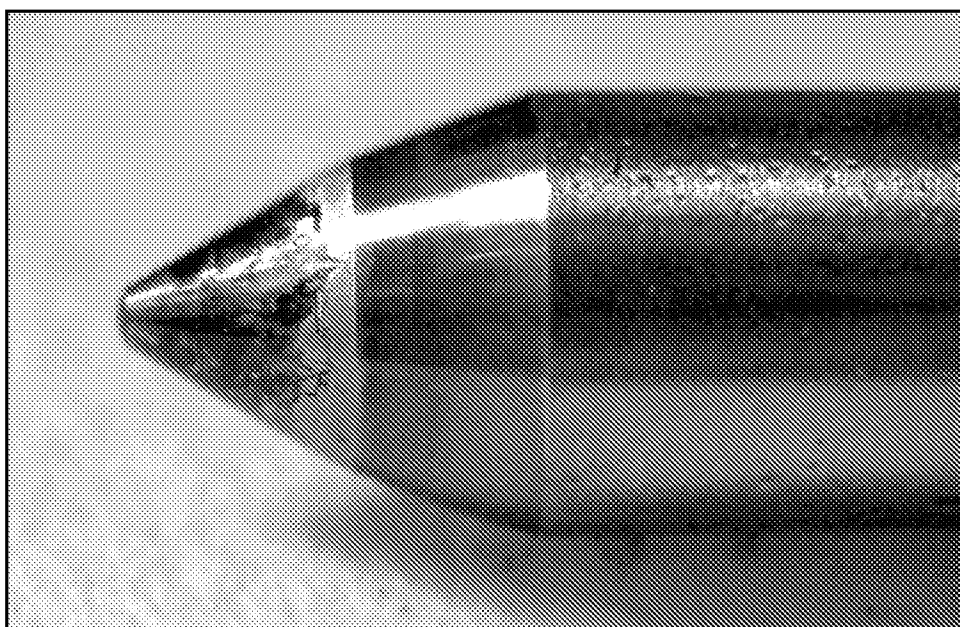


FIG. 9 (PRIOR ART)