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**OASMAA et al.**(10) **Pub. No.: US 2012/0285079 A1**(43) **Pub. Date: Nov. 15, 2012**(54) **PROCESS FOR STABILIZING FAST  
PYROLYSIS OIL, AND STABILIZED FAST  
PYROLYSIS OIL****Publication Classification**(51) **Int. Cl.**  
**C10L 1/185** (2006.01)(52) **U.S. Cl.** ..... **44/437**(57) **ABSTRACT**

A process for stabilizing pyrolysis oil includes hydrogenating fast pyrolysis oil with hydrogen reactant in the presence of ruthenium metal catalyst at a temperature of at least about 70° C. and at a pressure of at least about 600 psig to form a hydrogenated fast pyrolysis oil exhibiting an increase in viscosity of less than 10% after accelerated stability testing at 80° C. for 24 hours. The resulting hydrogenated fast pyrolysis oil can be characterized as stabilized to viscosity increase, and can be provided as a bio fuel oil.

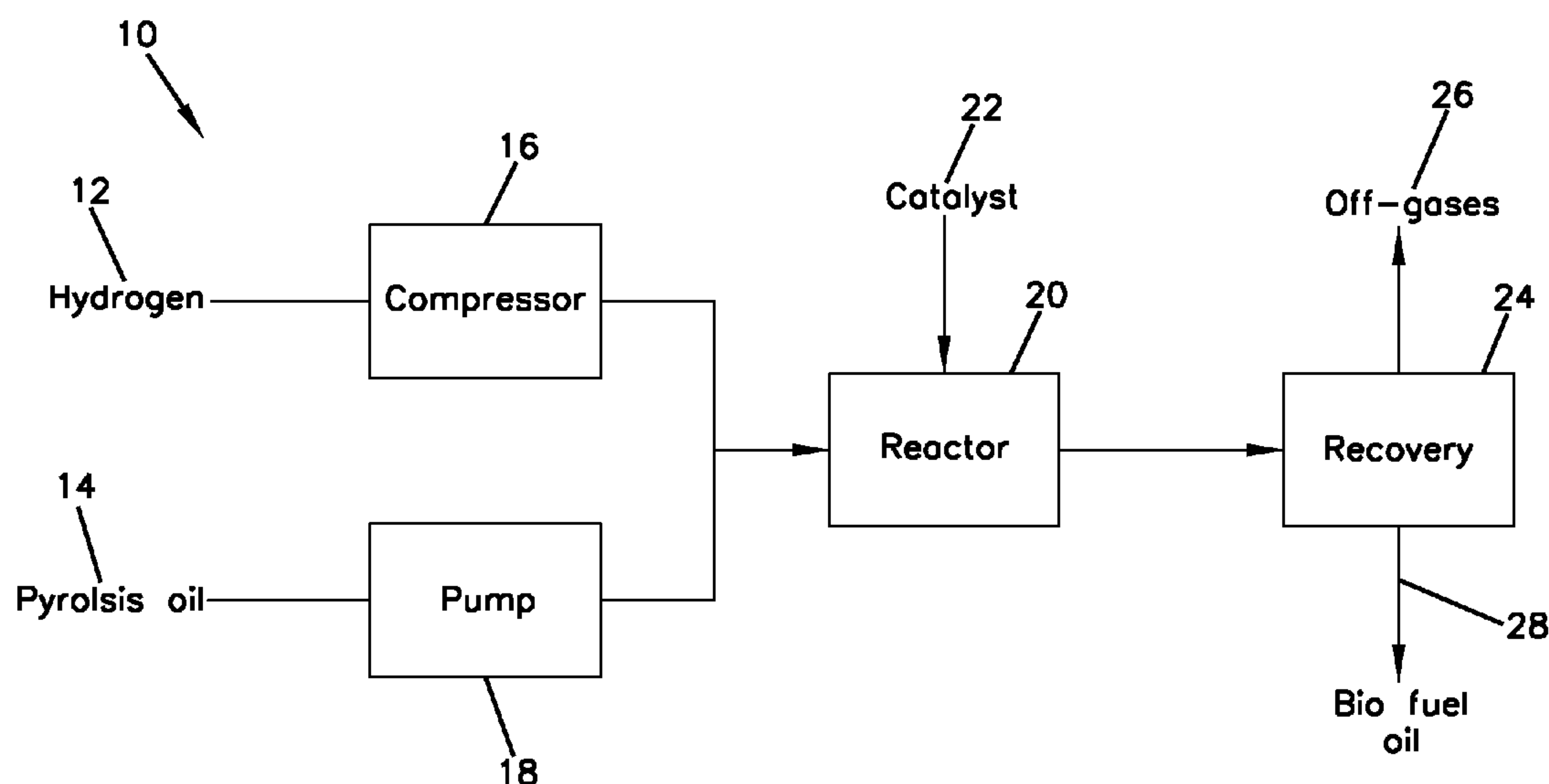
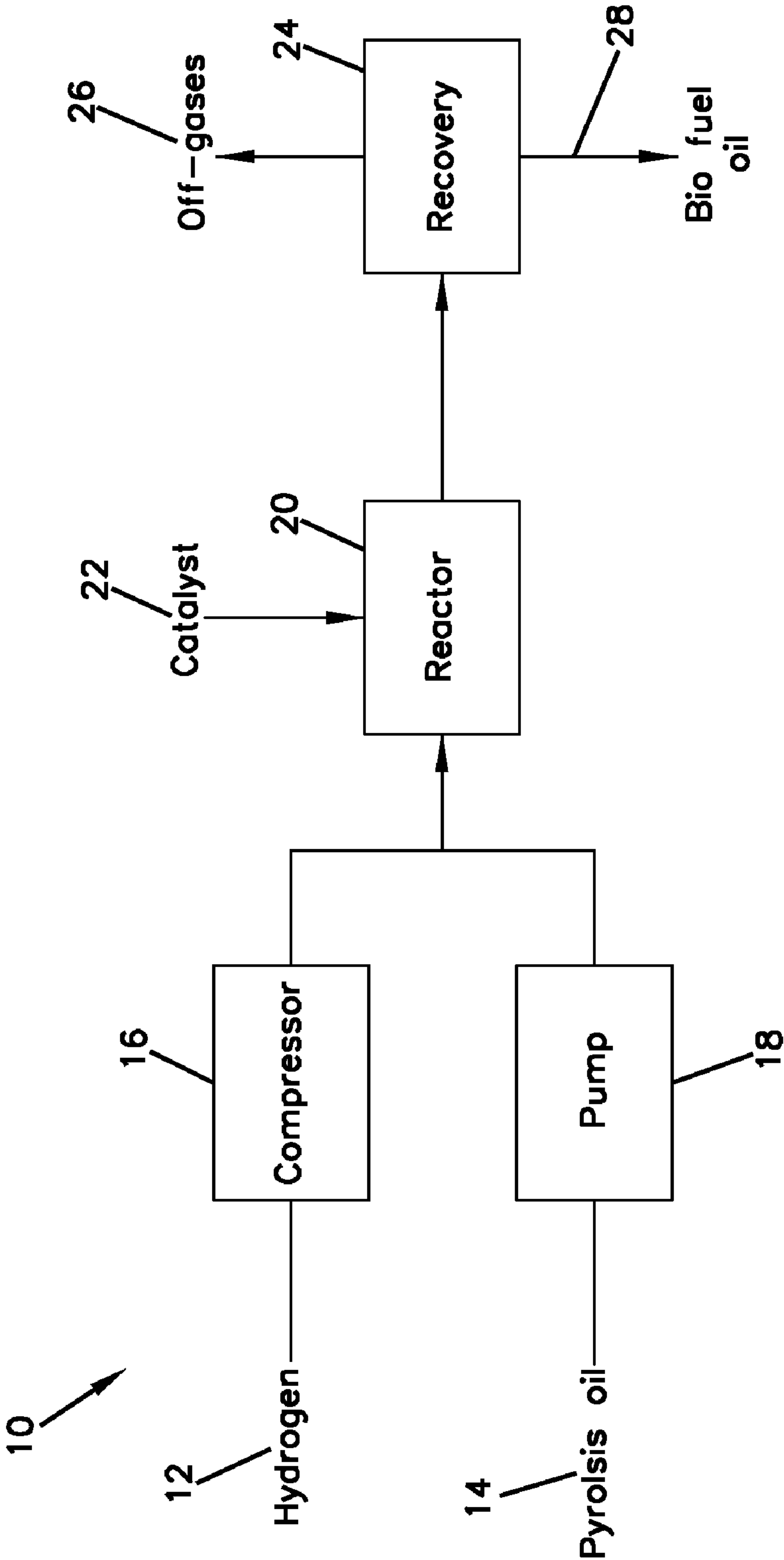
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FIG. 1





# PROCESS FOR STABILIZING FAST PYROLYSIS OIL, AND STABILIZED FAST PYROLYSIS OIL

## FIELD OF THE INVENTION

**[0001]** The invention is directed at a process for stabilizing fast pyrolysis oil, and to a stabilized fast pyrolysis oil. The process involves hydrogenating fast pyrolysis oil with a hydrogen reactant in the presence of a ruthenium metal catalyst. The resulting stabilized fast pyrolysis oil can be referred to as a stabilized hydrogenated bio oil, and can be used as a bio fuel oil.

## BACKGROUND

**[0002]** Vegetable oils and other plant derived oils have successfully been used as alternative, renewable heating oils for some time. However, relatively high costs prevent their wider use. In addition, vegetable oils and other plant derived oils are often prepared from a food source, and that make their use less attractive.

**[0003]** Fast pyrolysis oils are an alternative biomass derived fuel oil. Fast pyrolysis oils are typically produced from lignocellulosic materials which are not part of the food chain. Processes for forming fast pyrolysis oils are typically characterized by heating lignocellulosic materials to a temperature of about 400-600° C. for a short residence time (typically less than about three seconds) and in the absence of oxygen. If the temperature is too high or if the residence time is too long, secondary reactions tend to occur.

**[0004]** Fast pyrolysis oils have properties that make them generally unsatisfactory as fuel. For example, fast pyrolysis oils tend to be acidic and unstable to viscosity change resulting in an increase in molecular weight requiring special equipment such as pumps, vessels, and boiler systems for handling. A couple of solutions for the corrosiveness and instability of fast pyrolysis oils have been proposed. One proposed solution involves high-pressure hydrogenation of fast pyrolysis oils in order to upgrade the fast pyrolysis oils to a refinery feed, produce an oil fraction which would be similar to current boiler fuels. However, this proposal may be expensive. W. Baldauf, U. Balfanz, and M. Rupp, "Upgrading of flash pyrolysis oil and utilization in refineries," *Biomass and Bioenergy*, Volume 7, Issues 1-6, 1994, Pages 237-244, ISSN 0961-9534. Another proposed solution involves emulsion preparation of fast hydrolysis oils with fossil oils for preparing diesel fuel. M. Ikura, M. Stanculescu, and E. Hogan, "Emulsification of pyrolysis derived bio-oil in diesel fuel," *Biomass & Bioenergy* Vol. 24, Issue 3, 2003, Pages 221-232, ISSN 0961-9534. This proposal is technically applicable as boiler fuel, but has not been proven to be technically a feasible alternative to fossil oils. D. Chiamonti, et al., "Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines—Part 1: emulsion production," *Biomass and Bioenergy*, Volume 25, Issue 1, July 2003, Pages 85-99, ISSN 0961-9534. Another reference is B. Scholze, "Long-Term stability, catalytic upgrading, and application of pyrolysis oils," doctoral thesis, University of Hamburg, 2002.

**[0005]** Some work at low-temperature catalytic hydrogenation has suggested that such processing is not useful because it causes the same problems as high temperature storage.

## SUMMARY

**[0006]** A process for stabilizing fast pyrolysis oil is provided according to the invention. The process includes a step

of hydrogenating fast pyrolysis oil with hydrogen reactant in the presence of ruthenium metal catalyst at a temperature of at least about 70° C. and at a pressure of at least about 600 psig to form a hydrogenated fast pyrolysis oil exhibiting an increase in viscosity of less than 10% after accelerated stability testing at 80° C. for 24 hours.

**[0007]** A hydrogenated bio fuel is provided according to the invention. The hydrogenated bio fuel includes a result of hydrogenating fast pyrolysis oil with hydrogen reactant in the presence of ruthenium catalyst at a temperature of at least about 70° C. and at a pressure of at least 600 psig to form a hydrogenated fast pyrolysis oil. The hydrogenated pyrolysis oil exhibits a stability to viscosity so that the viscosity increases, if at all, less than 10% after accelerated stability testing at 80° C. for 24 hours.

**[0008]** Catalytic hydrogenation at mild conditions can be used to process raw bio-oil, from fast pyrolysis of biomass, into a stable fuel oil which can resist viscosity increase as measured in an accelerated aging test. The hydrogenated fast pyrolysis oil can be used to replace mineral fuel oil in heating.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0009]** FIG. 1 is a schematic representation of process for hydrogenating pyrolysis oil.

## DETAILED DESCRIPTION

**[0010]** Fast pyrolysis oil is typically produced by heating lignocellulosic materials to a temperature of about 400-600° C. for a residence time of generally at least about 0.5 second and less than about three seconds in the absence of oxygen. Fast pyrolysis oil generally includes a mixture of several oils produced as a result of the thermal treatment of lignocellulosic materials. For convenience, the mixture of oils can be referred to as fast pyrolysis oil. Fast pyrolysis oil can contain a number of chemical compounds including, for example, acetic acid, methanol, aldehydes, ketones, furans, alkylphenols, and sugars. In addition, fast pyrolysis oil may contain nitrogen or sulfur compounds. An exemplary fast pyrolysis oil is available as a bio oil having CAS Registry Number 1207435-39-9.

**[0011]** Fast pyrolysis oil tends to be susceptible to chemical change during storage resulting in an increase in viscosity. The chemical change may occur as a result of reactions involving, for example, carbonyl groups, olefinic groups, or both carbonyl groups and olefinic groups. The increase in viscosity may occur as a result of an increase in the amount and molecular weight of the water-insoluble fraction as a result of the chemical changes during storage. In addition, the increase in viscosity may occur as a result of phase separation where the less water soluble phase becomes more viscous. This increase in viscosity may occur at temperatures typically encountered during storage in a warehouse, and may be accelerated at higher temperatures. A rapid temperature change can lead to phase separation of the oil into an aqueous-rich phase and an aqueous-deficient phase. An increase in viscosity may render the pyrolysis oil unsuitable for handling in conventional equipment including pumps, vessels, and boiler systems.

**[0012]** By controlling the hydrogenation conditions of the fast pyrolysis oil in the presence of a ruthenium catalyst, the fast pyrolysis oil can be chemically modified to improve stability against viscosity increase without causing thermal degradation of the fast pyrolysis oil. The hydrogenation of the



fast pyrolysis oil can be referred to as a light catalytic hydrogen treatment because the hydrogenation conditions are carried sufficiently quickly and at a sufficiently low temperature to avoid significant thermal degradation of the fast pyrolysis oil. It is desirable to provide sufficient heat to promote hydrogenation while avoiding an amount of heat that would result in thermal degradation of the fast pyrolysis oil. In general, the temperature of the fast pyrolysis oil during hydrogenation can be at least about 70° C. While the temperature of the fast pyrolysis oil during hydrogenation can be provided below 70° C., the hydrogenation process may take longer in order to achieve the desired level of hydrogenation, or the reactor may be designed larger than desired. Because fast pyrolysis oil is temperature sensitive, the temperature of the fast pyrolysis oil during hydrogenation should be kept below about 100° C. in order to avoid undesired reactions. The temperature of the fast pyrolysis oil during hydrogenation can be provided at about 75° C. to about 90° C., about 78° C. to about 87° C., and about 80° C. to about 85° C. The fast pyrolysis oil can be subjected to an increased pressure in order to enhance the hydrogenation. While the hydrogenation can be achieved at atmospheric pressure, increasing the pressure tends to increase the rate of the hydrogenation process. Higher pressures are desired, but the cost of the process significantly increases at significantly high pressures. A desirable range of pressure for the hydrogenation process is about 600 psig to about 2000 psig. Additional pressure ranges include about 700 psig to about 1500 psig, and about 800 psig to about 1300 psig.

**[0013]** The rate of the fast pyrolysis oil through the hydrogenation reactor can be measured based on space velocity expressed as liters of fast pyrolysis oil through per liters of catalyst per hour (L/L/hr). The space velocity is typically referred to as a liquid hourly space velocity (LHSV). Based on the selection of the temperature and pressure of the hydrogenation process, the space velocity can be selected to provide the desired level of hydrogenation. In general, the space velocity can be selected as about 0.3 L/L/hr to about 1.0 L/L/hr. Preferably, the space velocity can be selected as about 0.4 L/L/hr to about 0.7 L/L/hr. Additional factors that can effect the selection of the space velocity include the size of the reactor and the activity of the catalyst, and the amount of the catalyst.

**[0014]** Now referring to FIG. 1, an exemplary schematic representation of a process for hydrogenating fast pyrolysis oil is shown at reference number 10. The schematic representation 10 includes a source of hydrogen 12 and a source of fast pyrolysis oil 14. The source of hydrogen 12 is conveyed via a compressor 16 to a reactor 20. The fast pyrolysis oil is conveyed via a pump 18 to the reactor 20. Also conveyed to the reactor 20 is a catalyst 22. Inside the reactor 20, the temperature, pressure, and residence time are controlled to provide the desired extent of hydrogenation of the fast pyrolysis oil. The residence time within the reactor 20 generally refers to the amount of time that the fast pyrolysis oil is subjected to hydrogenation. A more convenient expression that explains the amount of time that fast pyrolysis oil is subjected to hydrogenation is liquid hourly space velocity. The product from the reactor 20 is recovered at 24, and off-gases 26 are separated from the hydrogenated fast pyrolysis oil 28. The hydrogenated fast pyrolysis oil 28 can be referred to as stabilized fast pyrolysis oil or stabilized bio fuel oil. The process that occurs in the reactor 20 can be referred to as a hydrogenation reaction.

**[0015]** The catalyst useful in the hydrogenation reaction can be a ruthenium metal catalyst. The ruthenium metal catalyst can be a ruthenium metal catalyst on a support that withstands an aqueous environment. Exemplary supports that would withstand an aqueous environment include partially graphitized carbon in extrudate form, titania (rutile form) and zirconia (monoclinic form). The ruthenium metal catalyst can be referred to as a high activity ruthenium metal catalyst. An exemplary ruthenium metal catalyst on a partially, graphitized carbon extrudate support is available under the name BASF C3610.

**[0016]** The conditions of the hydrogenation reaction can be selected to provide the desired extent of hydrogenation of the fast pyrolysis oil. The conditions of the hydrogenation reaction include the temperature and pressure, the space velocity through the reactor, and the ruthenium metal catalyst. The extent of hydrogenation desired for stabilizing the fast pyrolysis oil can be referred to as lightly hydrogenated. By reducing the carbonyl content and by removing oxygen groups (deoxygenation), the stability of the fast pyrolysis oil can be improved. In addition, by lightly catalytically hydrogenating the fast pyrolysis oil, it is possible to avoid thermal treatment of the fast pyrolysis oil that may result in increased viscosity. In general, the carbonyl content of the fast pyrolysis oil can be reduced by at least 10% as a result of hydrogenation. Preferably, the carbonyl content of the fast pyrolysis oil can be reduced by at least 15% as a result of hydrogenation. The fast pyrolysis oil can be deoxygenated by at least 5% as a result of the hydrogenation. Preferably, the fast pyrolysis oil can be deoxygenated by at least 10% as a result of hydrogenation. The light catalytic hydrogenation can additionally be characterized as providing a sufficient hydrogenation to achieve the desired reduction in carbonyl content and oxygen groups while providing a hydrogenated fast pyrolysis oil that appears essentially the same as the non-hydrogenated fast pyrolysis oil. The hydrogenation reaction condition can be selected so that the hydrogenated fast pyrolysis oil appears or looks similar to the non-hydrogenated fast pyrolysis oil while providing enhanced stability to viscosity increase. In general, the reference to oils appearing or looking similar should be understood to mean that there is little obvious difference in physical appearance.

**[0017]** As a result of hydrogenating the fast pyrolysis oil, the resulting hydrogenated fast pyrolysis oil can exhibit an increase in viscosity of less than 10% (when the viscosity is measured at 40° C. and atmospheric pressure) after being subjected to an accelerated stability test where the oil is held at 80° C. for 24 hours. By hydrogenating the fast pyrolysis oil, the resulting hydrogenated fast pyrolysis oil can be stored as a bio fuel oil with reduced risk of handling problems when used in burner systems. This process utilizes a highly active hydrogenation catalyst, and as a result, this process uses less severe processing conditions than has been reported elsewhere for upgrading bio fuel oil by catalytic hydroprocessing. Furthermore, using the low severity processing conditions causes this process to require only a small amount of hydrogen reagent in the stabilization process. Because of these differences the cost of this process is favorable for both capital equipment investment and for operating costs, including hydrogen consumption. As a result, a stable bio-oil can be produced.

**[0018]** The following examples provide exemplary conditions of hydrogenating fast pyrolysis oil, and exemplary prop-



erties of the resulting hydrogenated fast pyrolysis oil. The following examples should not be treated as limiting the invention.

### Example 1

**[0019]** Continuous-flow process tests were performed with low-severity hydroprocessing to stabilize fast pyrolysis bio-oil. A pine fast pyrolysis bio-oil was used in each test. A ruthenium (7.8%) on carbon (partially graphitized extrudates) catalyst was used in a fixed bed with a trickle-flow (down flow) configuration. The tests were both performed at essentially the same temperature and pressure. After the treatment the recovered bio-oil products remained single phase with little obvious difference in physical appearance. Moisture and viscosity were measured. Carbon-13 nuclear magnetic resonance measurements were also made to determine changes in the chemical composition of the bio fuel oil. A thermal aging stability test was also performed.

**[0020]** The bio fuel oil was hydrogenated to a very slight degree. Carbonyl content was reduced slightly. The effect of space velocity was most noticeable for deoxygenation and hydrogen consumption; the effect being largest for the most severely processed bio fuel oil (low space velocity). The viscosity of the treated bio fuel oils was slightly reduced, but the significant effect was in the stability test result. The high space velocity treated bio-oil was significantly more stable than the untreated bio fuel oil, while the more severely treated bio-oil (low space velocity) was much more stable with only a slight increase in viscosity in the accelerated stability test.

TABLE 1

Results			
	pine bio fuel oil	Low LHSV	High LHSV
bed temperature, ° C.	—	83	81
bed pressure, psig	—	1218	1221
LHSV, L/L/hr	—	0.48	0.95
H <sub>2</sub> feedrate, L/hr	—	100	200
H <sub>2</sub> consumption, L/L	—	11.2	3.9
C=O content, % of C	4.2, 7.0	3.4	3.1
Deoxygenation	—	12%	1.6%
moisture, %	21.34, 21.76	22.75	21.97
viscosity, cSt@40° C.	22.9	15.8	20.8
Viscosity, cSt@40° C. after 24 hr@80° C.	32.55	16.6	26.45
viscosity increase, %	42	5.2	27

### Example 2

**[0021]** Other tests were performed in a similar manner to evaluate the effect of determine of lower temperature processing. Both a pine bio fuel oil and forest residue bio fuel oil were treated at the same low space velocity of 0.45. The products produced at 600 psig or 600 psig and 70° C. resulted in significantly less stabilized products based on the accelerated stability test. It was also noted that different bio-oil sources resulted in the same trends of stability improvement but at different levels of improvement.

TABLE 2

Results			
	After treatment Viscosity	Treated bio-oil After aging Viscosity	Increase in, % Viscosity
VTT Pine Bio-Oil 70° C./ 600 psig H <sub>2</sub>	22.1	25.3	14.8
VTT Pine Bio-Oil 82° C./ 600 psig H <sub>2</sub>	20.0	22.2	10.6
VTT Pine Bio-Oil 82° C./ 1200 psig H <sub>2</sub>	19.4	19.8	2.3
VTT Forest Pyrolysis Oil 70° C./ 600 psig H <sub>2</sub>	22.5	25.6	13.6
VTT Forest Pyrolysis Oil 82° C./ 600 psig H <sub>2</sub>	21.9	24.4	11.5
VTT Forest Pyrolysis Oil 82° C./ 1200 psig H <sub>2</sub>	21.5	23.8	10.5

**[0022]** The above specification, examples and data provide a complete description of the manufacture and use of the composition of the invention. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

We claim:

1. A process for stabilizing fast pyrolysis oil comprising:
  - (a) hydrogenating fast pyrolysis oil with hydrogen reactant in the presence of ruthenium metal catalyst at a temperature of at least about 70° C. and at a pressure of at least about 600 psig to form a hydrogenated fast pyrolysis oil exhibiting an increase in viscosity of less than 10% after accelerated stability testing at 80° C. for 24 hours.
2. A process according to claim 1, wherein the pyrolysis oil comprises a result of heating lignocellulosic materials to a temperature of about 400° C. to about 600° C. for less than three seconds.
3. A process according to claim 1, wherein the step of hydrogenating fast pyrolysis oil comprises hydrogenating fast pyrolysis oil at a temperature of about 70° C. to about 100° C.
4. A process according to claim 1, wherein the step of hydrogenating fast pyrolysis oil comprises hydrogenating pyrolysis oil at a temperature of about 75° C. to about 90° C.
5. A process according to claim 1, wherein the step of hydrogenating fast pyrolysis oil comprises hydrogenating pyrolysis oil at a pressure of about 600 psig to about 2000 psig.
6. A process according to claim 1, wherein the step of hydrogenating fast pyrolysis oil comprises hydrogenating pyrolysis oil at a pressure about 700 psig to about 1500 psig.
7. A process according to claim 1, wherein the space velocity, expressed as liters of the fast pyrolysis oil per liter of the ruthenium catalyst per hour is about 0.3 L/L/hr to about 1.0 L/L/hr.
8. A process according to claim 7, wherein the space velocity is about 0.4 L/L/hr to about 0.7 L/L/hr.
9. A process according to claim 1, wherein the step of hydrogenating fast pyrolysis oil comprises hydrogenating fast pyrolysis oil to provide a reduction of carbonyl content by at least 10%.
10. A process according to claim 1, wherein the step of hydrogenating fast pyrolysis oil comprises hydrogenating fast pyrolysis oil to provide a deoxygenation by at least 5%.

**11.** A hydrogenated bio fuel comprising a result of hydrogenating fast pyrolysis oil with hydrogen reactant in the presence of ruthenium metal catalyst at a temperature of at least about 70° C. and at a pressure of at about 600 psig, the hydrogenated fast pyrolysis oil exhibiting a stability to viscosity increase of less than 10% after accelerated stability testing at 80° C. for 24 hours.

**12.** A hydrogenated bio fuel according to claim 1, wherein the pyrolysis oil comprises a result of heating lignocellulosic materials to a temperature of about 400° C. to about 600° C. for less than three seconds.

**13.** A hydrogenated bio fuel according to claim 1, wherein fast pyrolysis oil has been hydrogenated at a temperature of about 70° C. to about 100° C.

**14.** A hydrogenated bio fuel according to claim 1, wherein the fast pyrolysis oil has been hydrogenated at a temperature of about 75° C. to about 90° C.

**15.** A hydrogenated bio fuel according to claim 1, wherein the fast pyrolysis oil has been hydrogenated at a pressure of about 600 psig to about 2000 psig.

**16.** A hydrogenated bio fuel according to claim 1, wherein the fast pyrolysis oil has been hydrogenated at a pressure about 700 psig to about 1500 psig.

**17.** A hydrogenated bio fuel according to claim 1, wherein the hydrogenated fast pyrolysis oil exhibits a carbonyl content reduction by at least 10% compared to the fast pyrolysis oil prior to hydrogenation.

**19.** A hydrogenated bio fuel according to claim 1, wherein the hydrogenated fast pyrolysis oil exhibits a deoxygenation by at least 5% compared to the fast pyrolysis oil prior to hydrogenation.

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