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(54) **USE OF WELL MIXED, BACKMIXED  
REACTORS FOR PROCESSING OF  
UNSTABLE BIO FEEDSTOCKS**

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(57) **ABSTRACT**

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In the present invention, pyrolysis oil is processed in a well mixed or a back mixed reactor to prevent the plugging up of a reactor that otherwise occurs. The pyrolysis oil can then be further upgraded in a hydroprocessing reactor through use of an appropriate catalyst.

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# USE OF WELL MIXED, BACKMIXED REACTORS FOR PROCESSING OF UNSTABLE BIO FEEDSTOCKS

## CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from Provisional Application No. 61/319,019 filed Mar. 30, 2010, the contents of which are hereby incorporated by reference.

## BACKGROUND OF THE INVENTION

[0002] The present invention generally relates to methods for producing biofuels, and more particularly relates to methods for producing biomass-derived pyrolysis oils having increased phase stability.

[0003] The use of biofuels is of growing interest due to an increased environmental awareness. Biomass-derived pyrolysis oils obtained from the pyrolysis of biomass are considered to be a promising biofuel. Biomass-derived pyrolysis oils have the potential to replace up to 60% of transportation fuels thereby reducing the dependency on conventional petroleum and reducing its environmental impact.

[0004] Fast pyrolysis is a process in which organic materials are rapidly heated to 450° to 600° C. in the absence of air. Under these conditions, organic vapors, pyrolysis gases and char are produced. The pyrolysis gases contain small amounts of reducing gases, such as hydrogen, carbon monoxide, etc. The vapors are condensed to biomass-derived pyrolysis oil. Pyrolysis of biomass under conditions of such rapid heating and short reactor residence times can produce low-viscosity, single-phase biomass-derived pyrolysis oil. Most projected uses of biomass-derived pyrolysis oil require that it retain these initial physical properties during storage, shipment and use. Pyrolysis is the chemical decomposition of condensed substances by heating, that occurs spontaneously at high enough temperatures. Pyrolysis is a special case of thermolysis, and is most commonly used for organic materials, being then one of the processes involved in charring. This chemical process is heavily used in the chemical industry, for example, to produce charcoal, activated carbon, methanol and other chemicals from wood, to convert ethylene dichloride into vinyl chloride to make PVC, to produce coke from coal, to convert biomass into syngas, to turn waste into safely disposable substances, and for transforming medium-weight hydrocarbons from oil into lighter ones like gasoline. These specialized uses of pyrolysis may be called various names, such as dry distillation, destructive distillation, or cracking

[0005] Pyrolysis differs from other high-temperature processes like combustion and hydrolysis in that it does not involve reactions with oxygen, water, or any other reagents. However, the term has also been applied to the decomposition of organic material in the presence of superheated water or steam (hydrous pyrolysis), for example in the steam cracking of oil.

[0006] Pyrolysis is the basis of several methods that are being developed for producing fuel from biomass, which may include either crops grown for the purpose or biological waste products from other industries.

[0007] Although synthetic diesel fuel cannot yet be produced directly by pyrolysis of organic materials, there is a way to produce similar liquid ("bio-oil") that can be used as a fuel, after the removal of valuable bio-chemicals that can be used as food additives or pharmaceuticals. Higher efficiency

is achieved by the so-called flash pyrolysis where finely divided feedstock is quickly heated to between 350° and 500° C. for less than 2 seconds.

## DESCRIPTION OF THE INVENTION

[0008] The present invention involves a process of upgrading a pyrolysis oil in which pyrolysis oil is sent to a well-mixed reactor or a back-mixed reactor to produce an upgraded pyrolysis oil.

[0009] Bio-based feedstocks, particularly pyrolysis oils, are unstable during processing. The instability may be thermal, chemical, or physical. These pyrolysis oils are difficult to hydroprocess due to formation of solids. This instability may be caused by high temperature excursions at the reactor inlet for an exothermic reaction, by depletion of reactants such as hydrogen needed to stabilize reactive intermediates, high concentrations of reactants which condense to form solids, or phase instability. These conditions may lead to precipitation of solids and reactor plugging. A well-mixed or backmixed reactor has uniform concentration and temperature throughout the reactor. Consequently, thermal and chemical instability are unlikely. Well mixed, or back-mixed reactors include stirred tank reactors, plug flow reactors with recycle, slurry reactors, as well as gaslift or jet reactors, all of which are well known to those skilled in the chemical arts.

[0010] The purpose of the first reactor is to process the feedstock to the point that its plugging propensity is reduced. Hence, the reactive species are reduced. The first reactor also needs to achieve the goal of metals removal. The reason for doing this in a backmixed reactor is to avoid plugging and also to potentially remove catalyst which has been loaded with metals. The effluent from the first feedstock now is routed to a fixed bed reactor, in which a more conventional processing approach can be taken. The catalyst used here is a more conventional deoxygenation/hydroprocessing catalyst.

## EXAMPLE 1

[0011] A feed comprising Pyrolysis Oil was tested in an autoclave reactor to simulate a backmixed reactor. A 300 cc autoclave was charged with 50 cc of feed and 10% by feed weight of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. After pressure testing, the autoclave was stirred at 300 to 500 rpm and pressurized with hydrogen to 8274 kPa (1200 psig). The temperature was ramped to the target and held for 2 hours. After cooling and depressurizing, the reactor, a two-phase liquid product, was removed from the reactor and analyzed. An equivalent space velocity was calculated based on the volume of feed and catalyst and the reaction time.

## EXAMPLE 2

[0012] The same feed was tested in a tubular reactor to simulate a plug flow reactor. The reactor tube was loaded with 15 cc of the same Pd/Al<sub>2</sub>O<sub>3</sub> catalyst and 45 cc of an alumina diluent and a metal spacer to occupy the void volume in the reactor. The loaded reactor was mounted in a furnace and pressure tested. The catalyst was pretreated with 5 to 10 cc/min of flowing hydrogen at ambient temperature. The reactor temperature was increased to 200° C. for 1 hour and then to 400° C. for 1 hour. The reactor was cooled to the target temperature and feed was cut in to the reactor at the target rate for 1 hr<sup>-1</sup> space velocity. The reactor was run overnight and a two-phase liquid product was collected throughout the run and analyzed.



	Example 1	Example 2
Temperature, ° C.	150	170
Pressure, kPa (psig)	10,340 (1500)	5,171 (750)
Space velocity, hr <sup>-1</sup>	2.7	1
Top Phase amount, vol-%	56	71
Top Phase, carbon, wt-%	20.7	20.9
Top Phase, hydrogen, wt-%	8.8	9.1
Bottom Phase, vol-%	44	29
Bottom Phase, carbon, wt-%	48.7	54.0
Bottom Phase, hydrogen, wt-%	8.0	6.9

[0013] The pressure for Example 1 was based on the start of the experiment and decreased during the run as hydrogen was consumed. The table shows that at less severe conditions (higher space velocity, lower temperature), an equivalent product was produced in Example 1, the backmixed system.

1. A process of upgrading a pyrolysis oil comprising sending said pyrolysis oil to a well-mixed reactor or a back-mixed reactor to produce an upgraded pyrolysis oil.

2. The process of claim 1 further comprising sending said upgraded pyrolysis oil to a reactor to further upgrade said upgraded pyrolysis oil.

3. The process of claim 1 wherein metals are removed from said pyrolysis oil in said well-mixed reactor or said back-mixed reactor.
4. The process of claim 1 wherein reactive species are removed from said pyrolysis oil in said well-mixed reactor or said back-mixed reactor.
5. The process of claim 2 wherein said upgraded pyrolysis oil is reacted with a catalyst in said reactor to cause said upgraded pyrolysis oil to be deoxygenated/hydroprocessed within said reactor.
6. The process of claim 1 wherein said upgraded pyrolysis oil is less likely to result in precipitation of solids and plugging of a reactor than a pyrolysis oil that has not been upgraded.
7. The process of claim 1 wherein said pyrolysis oil is subjected to hydroprocessing within said well mixed or said back-mixed reactor.
8. The process of claim 1 wherein said well-mixed or back mixed reactor is selected from the group consisting of stirred tank reactors, plug flow reactors with recycle, slurry reactors, gas-lift reactors and jet reactors.

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