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(54) Title: SELECTIVE CATALYTIC THERMOCONVERSION OF BIOMASS AND BIO-OILS

(57) Abstract: A process is disclosed for the catalytic conversion of solid biomass to bio-oil. In a first step, solid biomass is converted to bio-crude in the presence of a basic catalyst. In a second step the bio-crude is subjected to catalytic cracking in the presence of an acidic catalyst. The first step and the second step may be carried out simultaneously or sequentially. The process produces bio-oil of high quality, as evidenced by its low Total Acid Number (TAN).



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SELECTIVE CATALYTIC THERMOCONVERSION OF BIOMASS AND BIO-OILS

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates generally to a two-step process for preparing a bio-oil from solid biomass, and more particularly to a process using a basic catalyst in the first step and an acidic catalyst in the second step.

[0002] 2. Description of the Related Art

[0003] The use of a variety of solid inorganic materials as catalysts in gasification processes of solid fuels, such as coal and biomass goes back to the 1850s, when the catalytic activity of alkaline catalyst was described first in a patent letter in 1867. Later on, the importance of catalysts was further demonstrated in steam gasification of biomass, using, for example, potassium carbonate and tri-metallic transition metal catalysts supported on silica matrix.

[0004] Calcium oxide (lime) was found to increase the carbon conversion of wood and the net BTU recovery in gasification cations. Further, the conversion rate was increased, giving higher throughputs, while the reaction temperature was lowered, resulting in a greater efficiency. In particular, the use of calcium carbonate was found to increase the liquid organic yield.

[0005] Related to pyrolysis processes are the flaming and smoldering combustion processes, wherein the flaming combustion involves the gas phase oxidation of the pyrolysis products, and smoldering combustion involves the combustion of residues remaining after evaporation of the volatile components.

[0006] The kind of pathways, rates of conversion and yields are strongly affected by the heating conditions and the presence of inorganic matter.

[0007] Pyrolysis of cellulose involves two alternative pathways, one at lower temperature involving the decomposition of the glycosyl units to char, H₂O, CO, CO₂; and another at higher temperatures involving the depolymerization of the glycosyl units to volatile oily (tarry) products.

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[0008] The addition of flame-retardants to cellulosic materials promotes reactions that produce CO, CO₂, H₂O and char, while reducing the amount of volatile organic tarry products.

[0009] Early work on the kinetics and mechanisms of these reactions using cellulosic materials and inorganic additives as flame retardants was based on measurements obtained by Thermo-gravimetric analysis (TGA) (See F. Shafizadeh, J. Appl. Pyrolysis 6 (1984) 217-232; and M.J. Antal, Ind. Eng. Chem. Res. (1995) 34, 703-717). In general, the kinetics, mechanisms, yields and types of products of the pyrolytic processes depend strongly on the composition of the biomass, pretreatments, heating conditions and atmosphere, wherein the process is conducted and catalyst present.

[0010] In their original pioneer work, Shafizadeh and co-workers used Thermo-gravimetric analysis (TGA); thermal evolution (TEA); evolved gas analysis (EGA); and differential thermal analyses (DTA) to determine the kinetics and mechanisms of the thermal and thermo-catalytic conversions of cellulosic biomaterials. (See Cellulose Chemistry and Its Application, T.P. Nevell and S.H. Zeronian (Eds), Chapter 11, "Thermal degradation of cellulose", Ellis Horwood Ltd (1985) p 266) They showed that the main biomass components (cellulose, hemicellulose and lignin) undergo chemical/physical changes at different temperatures and at different rates. Furthermore, they showed that the addition of inorganic components, in general, lowers the temperature of the thermo-catalytic conversion as determined by the DTA and EGA analysis.

[0011] Additionally, the presence of inorganic compounds, whether indigenous or added, selectively promotes the formation of char at the expense of tarry oils.

[0012] There is a considerable amount of research work published on the kinetics of biomass decomposition in pyrolysis processes for the production of organic liquids. (See Antal, M., In Adv. in Solar Energy Vol. 2, Amer. Solar Energy Soc., NY, 1983)

[0013] A simplified model proposed originally by Shafizadeh describes the decomposition of biomass taking place first through primary reactions producing gas, tar (oil) and char, and subsequently the tar (oil) undergoes secondary reactions

producing gas and char. These reactions take place in parallel, thus complicating the kinetic model for biomass thermal degradation. (See F. Shafizadeh and W.F. DeGroot, "Combustion Characteristics of Cellulosic Fuels" in Thermal Uses and Properties of Carbohydrates and Lignins, Academic Press (1976))

[0014] Work reported later on showed that, if a high concentration of inorganic compounds (salts) is present during pyrolysis, the conversion route follows a mechanism that enhances ring fragmentation, yielding higher amounts of lower molecular weight compounds, for example, hydroxyacetaldehyde. When low concentrations of inorganic salts are present on the biomass during pyrolysis, the mechanism of degradation involves a depolymerization producing high molecular weight compounds, such as levoglucosan and fructose. Accordingly, the maximum degradation temperature depends on the amount of metals present on the biomass. (See Linden, et al., Chem. Eng. Comm. 1988, 65, 207-221)

[0015] Feldmann, et al. showed that adding ash or calcium oxide to lignocellulosic wood biomass prior to pyrolyzing that mixture increases the yield of volatile organic liquids. Both the wood-ash and calcium oxide decreased the yield of the char and increased the yield of the organic liquids. (See Amer. Chem. Soc., Symp. Ser. No. 144, ACS, Washington, DC, 1982)

[0016] The work of Hsisheng Teng and Yun-Chow Wei is of particular interest. (See Ind. Eng. Chem. Res. 1998, 37, 3806-3811) These authors used rice hull biomass in their pyrolysis studies. Using a high resolution DTG analysis technique, they were able to dissect the evolution of volatile materials into three individual components, that is, the lowest temperature (about 350 K) corresponding to the decomposition involving moisture volatilization, next at higher temperatures were the decompositions of the hemicelluloses and cellulose and, finally, at the highest temperature was the decomposition of lignin.

[0017] Another interesting finding of Hsisheng was an observed increase in the organic volatile yields, and a decrease of the char yield, when the rice-hulls were washed with water before pyrolysis. At the same time, the maxima of the decomposition peaks shifted to higher temperatures. The increase in the temperature

where the peaks occurred, as well as the increase in the activation energies of the volatilization, was attributed to the washing process, which removed indigenous inorganic salts that are known to decrease the decomposition peak temperatures when present in the biomass and act as catalysts in the thermo-degradation process of the biomass. Further, it was observed that the yield of the volatile organics was increased, while the yield of the residue char was decreased. These changes were due to removal of soluble organic matter by the washing, which during pyrolysis reacts with other components to form chars.

[0018] Gray, R., et al., in their work used a wood-derived material that was pyrolyzed in a fluidized bed reactor operated in a nitrogen atmosphere at different temperatures. (See Ind. Eng. Chem. Process Dev., Vol. 24, No. 3 (1985) 646-65) They acid-treated the samples as well as ion exchanged them with a calcium salt. They measured the yield of gases, aqueous and tar (oily) products, at three different pyrolysis temperatures. Both the acid-treated and calcium exchanged samples gave higher tar yields (organic, volatile compounds) than the untreated samples, which gave increased yields of water, char, and gases.

[0019] Zaror, C.A. et al., studied the char formation in the catalytic pyrolysis of biomass using different kinds of wood, as such, and impregnated with alkaline salts, which were pyrolyzed in a Thermo-gravimetric balance and also in a Gray-King Retort. (See Fuel, (1985), Vol. 64, 990-994) Their data show that the salt-impregnation caused the temperature at which the peak of the maximum mass loss is located to decrease, and all the weight loss curves were shifted to lower temperatures. This confirmed previous work indicating the decrease of the decomposition temperature that was caused by contacting biomass with inorganic salts, while at the same time enhancing devolatilization and an increase of the weight loss at lower temperature. Further, they observed that these effects are more pronounced when the biomass is impregnated with sodium and potassium carbonates. Most interesting are their data showing that when the carbonates (K and Na) impregnated feed samples (after impregnation) were washed with water before being subjected to the pyrolysis,

they produced much less char and gases and at lower decomposition peak-temperatures.

[0020] Varhegyi, G., et al., have studied the pyrolytic devolatilization of cellulose and sugar cane bagasse. (See *Energy & Fuels* (1988) 8, 267-272) The samples were impregnated with $MgCl_2$, $NaCl$, $FeSO_4$, and $ZnCl_2$ catalysts. The authors used a sophisticated experimental equipment arrangement by combining the Thermo-gravimetric and Mass Spectrometric instruments, and operating in a continuous simultaneous mode. In general, their data show substantial changes in yields and product distribution, as well as lowering the temperature of the weight-maximum loss peaks, as a result of catalyst impregnation.

[0021] DeGroot, W, and Shafizadeh, F. reported on the thermal decomposition of different kinds of wood and the effects of metal salts (K and Ca) additives. (See *Fuel* (1988), Vol. 67, 345-361) In these studies, the pyrolysis of wood was conducted in a Differential Thermo-Gravimetric apparatus (DTG). The wood samples were treated with acid, ion-exchanged with K or Ca salts, or impregnated with these salts. One of their observations indicated that the lower temperature decomposition peak, which is assigned to the decomposition of hemicellulose, shifted to a lower temperature, indicating that indigenous (exchangeable) metals, or additive metals are interacting with the acidic groups of the hemicellulose, thus resulting in decreasing the thermal stability of the hemicellulose component of the wood biomass. Further, they observed that the addition of potassium increases the char yield, while it reduces the decomposition (devolatilization) temperature. To the contrary, the addition of calcium reduces slightly the char yield, while increasing the decomposition temperature.

[0022] In these studies the specific tar yields, and gases, were not measured, but only the complete char residues. However, it is expected that, in general, thermal biomass degradations in a pyrolytic processes that result in lower char yields, usually are accompanied by higher tar (organic liquids) yields.

[0023] Additionally, it was observed that the results obtained in the pyrolysis depended on the specific mode of application of the particular salt to the biomass

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chars. For example, potassium carbonate impregnated into the biomass decreased its decomposition temperature, while when the same salt is ion-exchanged it produces the opposite result.

[0024] Related studies were reported by W. DeGroot, et al where they conducted similar investigations involving the ion exchanging of metal ions on wood and measuring their effect on decomposition temperatures and yields of volatile products. (See J. Analytical & Applied Pyrolysis (1989) 16, 117-126) Their technique of measuring these effects involved a combination of DTA and gas-phase FTIR spectroscopy. The ion exchange was done using calcium and potassium acetate salts. Further, the indigenous metals from the wood were removed by acid treatments, resulting in reducing the yields of the volatile products. Potassium ions exchanged into the wood increased substantially the yield of carbon dioxide, while at the same time lowering the temperature of the decomposition peak. It was concluded that at least part of this excessive amount of carbon dioxide is derived from the thermal decomposition of cellulose.

[0025] In general, the samples that were acid treated first, and subsequently calcium or potassium exchanged, gave similar results to those obtained with the untreated materials. These results indicate the important role that the indigenous metals present in the wood play in determining the yields, products and decomposition temperatures of the wood during pyrolysis.

[0026] Raveendran, K, et al., conducted extensive work on the influence of mineral matter on the pyrolysis of different wood biomass. The experimental apparatus consisted of a dynamic TGA, and a pyrolysis unit. Biomass samples included high lignin and low lignin wood materials. Samples were pretreated (a) by acid-treatment to remove the natural minerals (indigenous) present in the wood, (b) the acid-treated samples were subsequently impregnated with metals, and (c) synthetic biomass samples prepared by mixing lignin, hemicellulose and cellulose in proportions similar to the compositions found in the natural biomass samples. In these experiments, the yields of gas, char volatiles and temperature of maximum decomposition were measured. The salts used for the impregnation included Na_2CO_3 , K_2CO_3 , ZnCO_3 ,

NaCl, KCl, ZnCl₂, HCl, NaOH, and were used to treat 13 natural biomass materials plus several synthetic samples. (See Fuel (1995), Vol. 74, No. 12, 1814-1816)

[0027] It was observed that all types of biomass, except three (which contained large amounts of lignin and K), after having been demineralized (by HCl treatment), when pyrolyzed, produced less char and gas and more volatiles. In all cases (except for biomass, from milled husk), the temperature of maximum devolatilization (peak) was increased by the removal of indigenous inorganic matter from biomass.

[0028] The authors attributed the exceptional behavior of coir pith, ground nut shell and rice husk to their high contents of lignin and potassium. Potassium is well known for its catalytic activity in char gasification, yielding large quantities of CO₂. Further, it was suggested that changes observed with the use of salt impregnations with different metal salts are due to the nature of the particular cation (i.e., Na, K, Zn, Ca, Mg) and not due to the anion.

[0029] Fahmi, R., et al, reported on the effect of alkali metals present or added to two kinds of grasses and two kinds of wood on their catalytic pyrolysis. (See R. Fahmi et al, Fuel, 86 (2007) 1560-1569; D.S. Scott et al, J. Anal. Appl. Pyrolysis, 54 (2001)169-176 ; and D.J. Nowakowski et al, Fuel 86 (2007) 2389-2402). They used TGA and pyrolysis-GCMS apparatus to measure the thermo-catalytic decomposition, product yields and kinds of products. Acid treatments (HCl) were used to remove the indigenous metals from the samples, which were milled to below 500 µm particle size. High resolution DTG measurements showed the individual peaks for the decomposition of hemicellulose (about 500 K) and the higher temperature (598 K) corresponded to the cellulose component decomposition, which is more thermally stable as it is crystalline, whereas the hemicellulose (semi-crystalline) is less thermally stable. Further, using this high resolution DTG analysis, the intensity of the individual peaks provided relative quantitative estimates of the concentration of the individual components in the biomass samples. For example, the acid pretreatment of Festuca grass resulted in a 900% increase in the yield of levoglucosan during pyrolysis.

[0030] Further, a good linear correlation was established in this work between the decrease of the temperature of maximum cellulose degradation (T_{\max} peak) with increasing metal content (K + Na), present in the char/ash. Similarly, a good correlation was established showing the increase in the char production with increasing metal content during pyrolysis for the acid-treated and untreated samples. It was concluded that the acid treatment that removed at least most of the metals resulted in decreasing the amount of char formed and increased the yield of organic liquids as well as improving its quality for use as a fuel. Other catalytic biomass pyrolysis studies, using different kinds of catalysts, are described in other publications. (See Lappas, A., et al., Fuel 81 (2002), 2087-2095; Samolada, M.C., and Vasalos, I.A., Fuel 70 (1991) 883-890; and Samolada, M.C., et al, Energy and Fuels, 14, (2000), 1161-1167)

[0031] U.S. Patent No. 3,926,947 describes a process in which cellulosic waste materials such as paper and newsprint are treated with an acidic fire retardant that enhances the yield of certain bio-oils during pyrolysis. The fire retardants claimed were: phosphoric acid, ammonium phosphates, ammonium sulphate, and zinc sulphate, which were impregnated on the biomass before subjected to pyrolysis.

[0032] U.S. Patent No. 5,807,952 teaches a process for converting lignins to phenolic compounds by pyrolyzing the lignin in the presence of a strong base like KOH. The lignin and potassium hydroxide powders were mixed and placed into a single stage quench reactor heated to 600°C. Vapors were analyzed with a mass spectrometer.

[0033] U.S. Patent No. 5,395,455 describes a process for producing anhydrosugars from lignin and cellulose containing biomass by pyrolysis, using a strong acid pretreatment of the biomass before pyrolysis. Besides claiming the acid-removal of the natural minerals from the biomass, the patent also claims that certain anions, such as sulphate, sulphite or nitrate, can be added to the acid-treated biomass by impregnation. Further, after the strong acid-treatment (digestion) of the biomass, soluble organic material can be separated and the residue then pyrolyzed.

[0034] Thus, there is a particular need for providing an improved process for the catalytic conversion of solid biomass to bio-crude, followed by the catalytic upgrading of bio-crude to bio-oil.

BRIEF SUMMARY OF THE INVENTION

[0035] The present invention addresses these problems by providing a process for the conversion of solid biomass, said process comprising the steps of:

- (i) heating the solid biomass while in contact with a basic catalyst to produce a bio-crude;
- (ii) cracking the bio-crude in the presence of an acidic catalyst to produce a bio-oil.

[0036] Another aspect of the invention comprises a method for the conversion of solid biomass as described above wherein the ash content of the biomass is reduced prior to step (i).

DETAILED DESCRIPTION OF THE INVENTION

[0037] Based on the information provided in the prior art, the different inorganic materials added to the biomass during gasification, combustion and pyrolysis processes can be classified into two categories (A & B).

[0038] Category A involves inorganic materials which enhance the decomposition of the raw biomass, which may act as catalysts involving C-O and C-steam reactions. Such basic catalysts that increase the rate of the solid raw biomass conversion will be referred to herein as Primary Catalysts, and include the Alkaline and Alkaline Earth salts, oxides, hydroxides, carbonates, hydroxyl-carbonates, etc.

[0039] Because typical raw biomass has an acidic nature and acts as a solid-acid, its interaction with basic materials (of the Primary Catalysts category) through some solid acid-base reaction, is enhanced by having the biomass and the Primary Catalyst in intimate contact.

[0040] Category B involves acidic inorganic materials that interact with the evolving organic gases and liquid products, which are produced *in-situ* from the

thermolysis of biomass. These kinds of acidic catalysts are referred to as Secondary Catalysts, some of which are similar to those used in cracking heavy petroleum feed-stocks. Examples of the Secondary Catalysts include solid super-acids, fluorinated transition metal oxides (i.e., F-doped aluminum oxides), acidic zeolites, acidic clays, alumina-titania, silica-alumina composites with or without zeolites, and so on.

[0041] To optimize the effectiveness of these two types of catalysts (additives) used in the thermolysis of biomass, like in pyrolysis processes, the Primary Catalyst must be allowed to react effectively and selectively with the solid raw biomass first, while subsequently the produced organic gases and liquids are allowed to react with the Secondary Catalyst before they undergo further interactions between themselves, with the solid biomass or with the char.

[0042] Examples of acidic types of Additives/Catalysts applied to biomass before and during thermoconversion.

[0043] US Patent 3,926,947, the disclosures of which are incorporated herein by reference, teaches the use of acidic salts, applied to cellulosic materials by impregnation, using solutions of phosphoric acid, ammonium phosphate, zinc sulphate and zinc phosphate. Other acidic fire-retardants have been applied to cellulosic materials before being subjected to pyrolysis or gasification processes. Such applications are referred to as chemical pretreatments.

[0044] Another category of inorganic catalysts that have been applied to biomass by impregnation from solutions, include the chloride and sulphate salts of zinc, magnesium, sodium and iron. Such applications are referred to as chemical pretreatments.

[0045] Still another category of solid acidic catalysts, primarily silicon-aluminates, specifically known FCC-type catalysts, non-zeolite FCC, FCC-Additives and catalysts containing ZSM zeolites, or MCM zeolites, have been used as particulate physical mixtures in pyrolytic and gasification conversion reactions. Such applications using different particulate components of biomass and catalysts, are referred to as physical mixtures.

[0046] Examples of basic types of Additives/Catalysts applied to biomass as solutions by impregnation or ion exchange

[0047] Ion exchange of potassium cations in the wood from solutions has shown decrease of the maximum decomposition temperature and increase in the char yield. Calcium ions exchanged into the wood increased the temperature of decomposition with only a small effect on the char yield. (See DeGroot, W.F., et al, Analyt. and Applied Pyrolysis (184), 6, 217-232.)

[0048] Impregnation of biomass with alkaline carbonates, in particular with sodium and potassium carbonates, showed decrease of the maximum temperature of decomposition (devolatilization) and increased weight loss rates at lower temperatures. Carbonates are more effective at causing such effects. (See Ind. Eng. Chem. Process Dev., Vol. 24, No. 3 (1985), 646-65)

[0049] Impregnation and demineralization of different types of biomass are described by W. DeGroot, et al in the J. Analytical & Applied Pyrolysis (1989) 16, 117-126), where salts of zinc and potassium chlorides as well as potassium and zinc carbonates were impregnated on biomass, and the resulting volatiles, gas, liquid and char, were measured.

[0050] Further studies have been conducted involving impregnation of biomass with sodium basic compounds (sodium hydroxide, carbonate, silicate) and sodium chloride, and the impregnated samples were pyrolyzed. Additionally, acidic compounds such as titania and HZSM zeolites, were applied on biomass. All sodium compounds lowered the temperature of the devolatilization of biomass and the hydroxide and carbonate had the most effect, being the most basic. To the contrary, the acidic compounds of titania and zeolite HZSM had no effect. (See Wang Jun, et al., Thermochemica Acta 2006, 444, 110-114)

[0051] Examples of Solid Basic Catalysis Applied to Biomass before Thermoconversion

[0052] For catalytic conversion of biomass (wood), potassium carbonate was demonstrated to be an effective catalyst for biomass gasification reactions as it lowers

the gasification temperature, increases the gasification rates, increases gas yields and increases the heat content of the fuel gas produced. (See Ross, R.A., and Fong, P., Ind. Eng. Prod. Res. Dev., 1981, 20, 197-203)

[0053] Flash pyrolysis in fluidized bed experiments were conducted for maximizing the organic liquid yield from biomass using lime and a nickel hydrogenation catalyst. The solid lime particles were mixed with woody sawdust and the physical mixture pyrolyzed at different temperatures. The addition of lime resulted in a lower temperature decomposition for maximum liquid yield and an increase of light hydrocarbon yields.

[0054] Additionally, the lime catalyst produced liquid organic products (tar) which contained higher carbon and less oxygen contents.

[0055] The reduction of the oxygen content in the oils (tar) was explained as being due to a greater production of CO and CO₂. Therefore, the best quality of oils (tar) was produced at the point of maximum yield. (See Scott, D.S., et al., Ind. Eng. Chem. Pro. Res. Dev., 1985, 24, 581-588)

[0056] Above references show, in general, that the addition of inorganic salts on biomass have a strong effect on the temperature of devolatilization of biomass during pyrolysis or gasification conditions as well as on the composition and yields of the gases, liquids, tar and char produced.

[0057] A simplified model of the various decomposition, cross-interactions and product formation pathways, involves a primary and a secondary stage. In the Primary Stage, primary liquids and primary char are being formed. In the secondary stage, primary liquids transform into tar, secondary char, and light pyrolysis products. These light hydrocarbon products, which include acids, esters, aldehydes and ketones act as catalysts to further auto-catalyze the breakdown of the primary liquids to lighter products.

[0058] These reactions proceed simultaneously and in a competitive fashion, and enhancement of one or the other can be accomplished by changing reaction conditions, biomass bulk accessibility, pyrolysis reactor configuration or catalysts.

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[0059] Having two kinds of catalysts, as, for example, an acidic and a basic type present in close contact with the biomass during thermoconversion, results in causing superimposed and competitive reactions that take place among the products and between the products and residual biomass/biomass remnants, thus all resulting in decreasing the yields of organic liquids as well as their quality.

[0060] This invention describes a two-step process that enhances the production of pyrolysis oils and improves their quality in terms of containing less oxygen, more carbon, being less acidic and having lower molecular weight.

[0061] Specifically, in the First Step, to achieve optimal thermoconversion of the biomass, the catalyst must be uniformly distributed on the surface or penetrated into the individual biomass particles. Impregnations, from solutions or from catalyst slurries, assisted with shear mechanical mixing, is much more effective in distributing homogeneously the catalyst on the surface of the individual biomass products than, for example, by simply mixing the biomass with the solid catalysts, or by co-milling the biomass with the catalyst.

[0062] Absorbing the catalyst into the bulk of the biomass using swelling techniques is an effective way to achieve optimum catalyst distribution, as described in patent application WO 2007/128800. Therefore, in the First Step, a "Biomass-Catalyst" [B-C] composite particle is prepared wherein the biomass and catalyst exist in intimate contact within the pores and on the biomass particle surfaces. The catalyst inorganic phase, a part of the B-C composite, having a higher heat capacity than the organic biomass phase, enhances (facilitates) the heat transfer and thus initiates the interaction of the catalyst species with the (organic) biomass at an earlier stage of the overall pyrolysis process.

[0063] Further, the basic catalyst effectively interacts with the biomass, which is acidic in nature, as both components exist in intimate contact while the biomass decomposes with the assistance of the basic catalyst. In simple terms, this can be envisioned as an "acid-base" reaction. Still further, while the basic catalyst is part of the "Biomass-Catalyst" composite, the light organic gases and tars produced in the flash pyrolysis are removed and thus have a lesser exposure towards the basic catalyst-

biomass composite, thus minimizing the cross and the back-reactions with the basic catalyst part of the biomass-catalyst composite particle.

[0064] Another beneficial function that the basic catalyst serves (being an integral part of the composite) is to neutralize the acids produced during the thermolysis of the biomass, which acids act as catalysts in reactions between the products and between the products and biomass. At the same time, such acidic neutralizations caused by the basic catalyst, increase the pH of the tars, so the tars having a higher pH are more suitable to be treated with an acidic type of cracking catalyst to be converted to light hydrocarbon products.

[0065] Additionally, the presence of the basic catalyst in contact with the biomass during the thermolysis results in tars having a lesser amount of oxygen content, resulting from reactions involving the catalyst metal (M) with the biomass with possible formation of intermediates involving M-O and M-OH bonds.

[0066] Another mode of operating the First-Step of the process involves using fine powders of the basic-catalyst and homogenously mixing the powder with the fine particles of biomass while heating the biomass to cause a softening of the biomass surface sufficient to allow the basic-catalyst particles to adhere to the biomass particles. This procedure does not use water, only the two fine particle powders are bonded together. This procedure is useful when water solutions or slurries of the basic-salt catalysts are not desirable. Steaming may optionally be used to facilitate the adhering process of the two solid particles.

[0067] Still another mode of operation of this invention involves contacting the biomass in the pyrolysis reactor with the fluidized bed of the heat carrier which contains a basic catalyst. Said basic catalyst may function also as a heat carrier and may consist of oxides, hydroxides, hydroxycarbonates, carbonates of the alkaline and alkaline earth metals, and mixtures thereof.

[0068] The Second-Step of the Process

[0069] The purpose of the Second-Step is to catalytically crack the freshly, instantly in-situ-generated tar with an acidic cracking type of catalyst before the tar components

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cross interact between themselves, and with the remnants of the biomass to form heavier organic compounds (tars) or chars.

[0070] Another objective of the second-step is, to the extent that it is physically/mechanically possible, to keep separate (with minimum superimposition), the reactions of the acidic catalyst with the nascent tars from the devolatilization of the biomass-catalyst composite.

[0071] Practical means of accomplishing this involve using the acidic catalyst as separate individual particles included in the fluidized bed, or introducing the acidic catalyst in the dilute phase zone of the pyrolysis reactor, wherein the freshly generated tar exists in higher concentrations.

[0072] In another mode of operation, the second-step of the process can be conducted in a separate reactor connected in line with the pyrolysis reactor.

[0073] Other embodiments of the invention involve the use of acidic catalyst as a heat transfer medium with or without the presence of sand.

[0074] The overall objective of this invention has two functions: (a) to selectively promote, first, the solid biomass-basic catalyst reaction and second by (b) promoting the tar/vapors-acidic catalyst reaction, while at the same time minimizing the overlapping and competing cross interactions between these two functions (a) and (b).

[0075] In another mode of operation of this invention, only the first-step of the overall process can be used to obtain the tar with the aid of a heat carrier, but without the second-step to upgrade the tars.

[0076] The overall process is flexible and provides a means to selectively optimize product yields and quality. For example, to maximize the yields of the bio oils, the acidic catalyst can be used in the second-step of the process, whereas in the first-step, a pretreated biomass can be used.

[0077] Examples of pretreated biomass material include:

[0078] Biomass that has been demineralized, for example by water or acid extraction;

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[0079] Biomass that has been torrefied /toasted by exposure to temperatures in the range of 80 to 300 °C;

[0080] Biomass that has been swollen without ion exchange;

[0081] Biomass that has been demineralized and then contacted with a basic catalyst;

[0082] Biomass that has been torrefied /toasted and contacted with a basic catalyst.

[0083] Calcium compounds applied to biomass, in contrast to the salts of alkali metals from Group I of the Periodic Table, do not lower the bio oil yields, and produce maximum yields at lower biomass decomposition temperatures, as do all other metals. However, the use of calcium compounds (i.e., lime, limestone, dolomite, etc.) has the additional advantage that the biomass (tar) produced contains less oxygen and higher amounts of carbon.

[0084] Since the calcium oxides, hydroxides, carbons, hydroxyl carbonates are strong basic catalysts, the acidity of the condensable liquids oily tars are less acidic and exhibit a low TAN.

[0085] It is important that the calcium catalyst is finely and uniformly applied to biomass particles, which is accomplished by applying a fine spray of the slurry to the small particle of biomass while it is being vigorously agitated or fluidized. Impregnation of the biomass small particles with slurries containing well dispersed in colloidal form the calcium compounds is another method of placing the calcium catalyst in intimate contact with the biomass before pyrolysis, as a first-step processing. Also, this can be accomplished in a kneader with spraying capability.

[0086] Further, the pretreated biomass with calcium-bearing catalyst can be pyrolyzed in a fashion that the acidic catalyst preferably is introduced to the pyrolysis reactor after the biomass has been thermolyzed, as, for example, in the dilute phase of the fluidized bed or in a second, in-line reactor, such as the stripper. This second-step processing is designed to achieve further upgrading of the bio oils (tars).

DESCRIPTION OF PREFERRED EMBODIMENTS

[0087] The process of the invention optimizes both the yield and the quality of bio-oil obtained in the pyrolytic conversion of solid biomass by providing a basic catalyst for catalyzing the conversion of the solid biomass to a liquid conversion product, and an acidic catalyst for upgrading the liquid conversion product.

[0088] For ease of reference the liquid conversion product is referred to as "bio-crude"; the upgraded bio-crude is referred to as "bio-oil". It should be noted that this nomenclature differs from many publications, which tend to refer to any liquid biomass pyrolysis product as bio-oil.

[0089] In one embodiment of the invention the basic catalyst and the acidic catalyst are both present during the biomass conversion reaction. If both catalysts are solid, chemical interaction of the two catalyst types with each other is minimized. This embodiment has the advantage that the bio-crude components are upgraded *in situ*, as they are formed.

[0090] In another embodiment of the invention the conversion step and upgrading step are conducted sequentially in the same reactor. Specifically, the solid biomass is initially contacted in the reactor with the basic catalyst alone; after at least part of the conversion to bio-crude has taken place, the acidic catalyst is introduced into the reactor.

[0091] The latter embodiment can conveniently be carried out in a fluid bed riser. Solid biomass particles and solid base catalyst particles are introduced near the bottom of the riser. The solid acid catalyst is introduced at a higher point in the riser, preferably at or above the mid-point of the riser.

[0092] In another embodiment of the process of the invention, the cracking step is carried out in a separate reactor, for example a stripper, a disengager or a cyclone located downstream from a fluid bed riser. Suitably the bio-crude is separated from unconverted biomass prior to being subjected to the cracking step.

[0093] It may be desirable to conduct the first step and the second step at different temperatures. For example, the conversion of the solid biomass may be carried out at

a temperature in the range of from 400 to 550 °C. The cracking of the bio-crude to bio-oil may be carried out at a lower temperature, for example in the range of from 350 to 450 °C. If the two steps are carried out in a riser, this can be accomplished by quenching the reaction mixture with cold acidic catalyst.

[0094] Conversely, it may be desirable to conduct the cracking step at a higher temperature than the conversion step. This can be accomplished by pre-heating the solid acid catalyst prior to addition to the reaction mixture.

[0095] In general, a lower cracking temperature results in a lower gas yield, and a heavier bio-oil. A higher cracking temperature results in a higher gas yield, and a lighter bio-oil.

[0096] In one embodiment of the invention the solid biomass material and the basic catalyst are mixed in the reactor. In this embodiment the basic catalyst can be used as a heat carrier, providing all or part of the heat for the endothermic conversion reaction.

[0097] In another embodiment of the invention the solid biomass and the basic catalyst are contacted with each other prior to entering the reactor. This pre-contacting may take place just prior to entering the reactor, or it may be done in a separate pretreatment step. The pretreatment step desirably comprises mechanical treatment, such as co-milling, co-grinding or co-kneading of the solid biomass and the basic catalyst.

[0098] An important aspect of the process of the invention is the high quality of the bio-oil produced by it. An important parameter for gauging the quality of a bio-oil is the Total Acid Number, or TAN, defined as the amount of KOH, in mg, required to neutralize 1 g of the bio-oil. Prior art processes typically produce bio-oils having a TAN above 50.

[0099] The bio-oils produced by the process of the present invention generally have a TAN of less than 40. The process can be optimized, for example by pre-treating the biomass, and/or by a judicious choice of reaction temperatures, to produce bio-oils having a TAN of less than 20.

[00100] As explained hereinabove, minerals naturally present in the solid biomass may interfere with the catalytic process. It is desirable to use biomass feedstocks for the process having an ash content of less than 5 wt%, preferably less than 2 wt%. This can be accomplished by selecting a biomass source having a naturally low level of ash, or by subjecting the biomass feedstock to an ash removal step. For example, indigenous salts can be effectively removed by extraction with an aqueous liquid.

[00101] The extraction step may comprise swelling the biomass with the aqueous liquid, and removing at least part of the aqueous liquid (which contains dissolved minerals from the biomass) by mechanical action. Examples of suitable mechanical action include pressing in a filter press or in a kneader.

[00102] Examples of suitable basic catalysts are disclosed in the prior art discussed hereinabove, the disclosures of which are incorporated herein by reference. Preferably the basic catalyst comprises a cation from Group I or Group II of the Periodic Table of the Elements.

[00103] The cation preferably is added in the form of its oxide, hydroxide, carbonate, or a combination thereof.

[00104] Preferred cations from Group I of the Periodic Table are Na and K. A preferred cation from Group II of the Periodic Table is Ca. Suitable examples of Ca-containing basic catalysts include lime and dolomite.

[00105] The acidic catalyst preferably comprises a solid acid. Suitable examples of solid acids include the acidic zeolites, such as HZSM zeolites, and H-Mordenites.

WHAT IS CLAIMED IS:

1. A process for the conversion of solid biomass, said process comprising the steps of:
 - (i) heating said solid biomass while in contact with a basic catalyst to produce a bio-crude;
 - (ii) cracking said bio-crude in the presence of an acidic catalyst to produce a bio-oil.
2. The process of claim 1 wherein step (i) and step (ii) are carried out simultaneously.
3. The process of claim 1 wherein step (i) and step (ii) are carried out sequentially.
4. The process of claim 1 wherein step (ii) is started after step (i) is partially completed, and before step (i) is fully completed.
5. The process of claim 3 wherein step (i) and step (ii) are carried out in the same reactor.
6. The process of claim 3 wherein step (i) and step (ii) are carried out in different reactors.
7. The process of claim 6 wherein step (i) is carried out in a fluid bed riser, and step (ii) is carried out in a stripper, a cyclone or a disengager downstream from said fluid bed riser.
8. The process of any one of the preceding claims wherein step (ii) is carried out at a lower temperature than step (i).
9. The process of any one of claims 1 – 7 wherein step (ii) is carried out at a higher temperature than step (i).
10. The process of any one of the preceding claims wherein said solid biomass material and said basic catalyst are mixed in said reactor for step (i).
11. The process of any one of claims 1 – 9 wherein said solid biomass material and said basic catalyst are mixed prior to entering said reactor of step (i).
12. The process of claim 11 wherein said solid biomass material and said basic catalyst are mixed in a pretreatment step comprising mechanical action.

13. The process of claim 12 wherein said mechanical action comprises co-milling, co-grinding, co-kneading, or a combination thereof.
14. The process of any one of the preceding claims wherein said bio-oil has a total acid number (TAN) of less than 40.
15. The process of claim 14 wherein said bio-oil has a total acid number (TAN) of less than 20.
16. The process of any one of the preceding claims wherein said solid biomass has an ash content of less than 5%.
17. The process of claim 16 wherein said solid biomass has an ash content of less than 2%.
18. The process of claim 16 or 17 wherein, prior to step (i), said ash content is lowered by extraction of indigenous salts with an aqueous liquid.
19. The process of claim 18 wherein said extraction of indigenous salts comprises swelling said solid biomass with said aqueous liquid, and removing at least part of said aqueous liquid from said solid biomass by mechanical action.
20. The process of any one of the preceding claims wherein said basic catalyst comprises a cation from Group I or Group II of the Periodic Table of Elements.
21. The process of any one of the preceding claims wherein said basic catalyst comprises an oxide, a hydroxide, a carbonate, or a combination thereof.
22. The process of claim 20 wherein said cation is K or Na.
23. The process of claim 20 wherein said cation is Ca.
24. The process of claim 23 wherein said basic catalyst is lime or dolomite.
25. The process of any one of the preceding claims wherein said acidic catalyst comprises a solid acid.
26. The process of claim 25 wherein said solid acid comprises a zeolite.
27. The process of claim 26 wherein said solid acid comprises HZSM or H-Mordenite.
28. The process of any one of the preceding claims wherein step (ii) is carried out in a fluidized bed reactor.

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29. The process of claim 3 wherein said bio-crude is separated from unconverted biomass prior to step (ii).

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/67488

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C10G 1/08 (2010.01)

USPC - 208/419; 44/606

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC - 208/419; 44/606

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 208/419; 44/606

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPTO WEST (PGPB,USPT,USOC,EPAB,JPAB), Google Patent: biomass, bio-oil, bio-crude, wood, rice hull, lignin, catalyst, alkaline, acid, reactor, fluidized bed, temperature, phosphoric acid, phosphate, sulfate, stripper, cyclone, vortex, disengager, cracking

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,266,083 A (HUANG) 05 May 1981 (05.05.1981), col 2, 15-24, 33-37; col 3, ln 1-34; col 4, ln 38-40, 45-49; col 5, ln 5-25; col 6, ln 10-16	1-9 and 29
Y	US 5,233,109 A (CHOW) 03 August 1993 (03.08.1993), col 1, 9-16; col 3, ln 1-7, 20-22, 43-49	1-9 and 29
Y	US 4,064,018 A (CHOI) 20 December 1977 (20.12.1977), col 4, ln 33-38; col 6, ln 38-54	2, 8/(2) and 9/(2)
Y	US 5,599,510 A (KAMINSKY et al.) 04 February 1997 (04.02.1997), col 12, ln 1-12	5, 8/(5) and 9/(5)

☐ Further documents are listed in the continuation of Box C.


* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 January 2010 (14.01.2010)

Date of mailing of the international search report

01 FEB 2010

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/67488

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 10-28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.