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(54) **Method of upgrading biomass pyrolysis liquids for use as fuels and as a source of chemicals by reaction with alcohols**

Verfahren zur Aufarbeitung von Pyrolyseölen zur Anwendung als Brennstoffe und als Ausgangsprodukt für chemische Produkte durch Reaktion mit Alkoholen

Procédé d'amélioration d'huiles de pyrolyse comme combustibles et comme produit de départ pour produits chimiques par réaction avec des alcools

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• **CHEMICAL ABSTRACTS, vol. 96, no. 18, 3 May 1982 Columbus, Ohio, US; abstract no. 96146001, POLK M. B.: "development of methods for the stabilization of pyrolytic oils." page 198; column right; XP002000127 & REPORT 1981 EPA600/2-81.201, POLK M.B.:**

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Description

[0001] This invention relates to a method of upgrading liquid products freshly obtained from the pyrolysis of biomass to chemically and thermally stabilize said products. In particular, a method is provided for modifying the liquid products from the pyrolysis of biomass by removing water therefrom and for converting aldehydic, ketonic and carboxylic compounds present therein to acetals, ketals and esters, respectively.

[0002] There has been a considerable effort over the past several years to develop pyrolysis processes for the conversion of ligno-cellulosic and other biomass to liquids for the express purpose of producing renewable liquid fuels suitable for use in boilers, gas turbines and diesel engines. The highest yields of liquids are obtained by condensation of the vapours from fast pyrolysis processes. These feature high heating rates and short vapour residence times. Typically, heating rates are of the order of 1000°C per second or greater to final temperatures in excess of 350°C and vapour residence times are less than three seconds. The other products consist of a solid char and permanent gases like carbon monoxide, carbon dioxide and methane.

[0003] In the following the said liquid product is referred to variously as the pyrolysate, pyrolytic oil or pyrolytic tar.

[0004] It is possible to attain the desired heating rates in a variety of apparatuses. These include fluidized beds, entrained beds, vortex reactors, pyrolytic mills, ablative pyrolysis reactors and so-called "rapid thermal processing" reactors (including circulating fluid beds) among other embodiments. Lower heating rates can be tolerated if vapour residence times are kept sufficiently small as obtained in vacuum pyrolysis processes. These various biomass pyrolysis technologies have been reviewed by A.V. Bridgwater and S.A. Bridge in "Biomass Pyrolysis Liquids Upgrading and Utilisation", A.V. Bridgwater and G. Grassi (eds.), Elsevier, London, 1991.

[0005] While the data provided in the subsequent description were obtained by flash pyrolysis in a fluidized bed, similar liquid and char pyrolysates can be obtained from all reactor systems which are characterized by high temperature and/or short residence times as pointed out by G. Underwood and R.G. Graham in U.S. Patent Number 4,994,297 (1991). For example, Table 5 of this reference shows that the results obtained by fluidized bed pyrolysis and reported earlier by D.S. Scott, [D.S. Scott and J. Piskorz in Bioenergy 84, Vol. III, H. Egneus and A. Ellegard (eds.), Elsevier, London, 1985] are comparable to those from the rapid thermal processing process.

[0006] Some typical yields obtained by fast pyrolysis of various biomass in a fluidized bed are shown in Table 1 below:

| Feedstock | Yields, Wt % of mf Feed | | | | | | |
|----------------|-------------------------|-------------|----------|-------------------------|--------------------|-----------------|-----------|
| | Poplar-Aspen Wood | Wheat Chaff | Hog Fuel | Sulfite Pulp Mill waste | Bleached Cardboard | Sorghum Bagasse | Peat Moss |
| Gas | 10.8 | 15.9 | 13.1 | 9.3 | 20.5 | 11.7 | 16.2 |
| Char | 7.7 | 17.6 | 31.8 | 19.5 | 3.8 | 13.4 | 26.3 |
| Water | 12.2 | 15.7 | 12.1 | 20.3 | 16.4 | 10.6 | 8.2 |
| Organic Liquid | 65.8 | 51.0 | 46.6 | 46.8 | 55.3 | 58.8 | 49.1 |

[0007] The use of these pyrolysis liquids as fuels for boilers, gas turbines and diesel engines is under investigation at present by various organizations. Unfortunately, they possess several characteristics which render such applications difficult or impractical. Some of these are as follows [J.C. Cassanova, "Biomass Pyrolysis Oil Properties and Combustion", Estes Park, September, 1994]:

(a) These liquids are chemically unstable and over time increases in viscosity and molecular weight at the same time that the water content increases, [S. Czernik, Proceedings, "Biomass Pyrolysis Oil Properties and Combustion", Estes Park, September, 1994]. The aging process is accelerated with increases in temperature, a fact which causes problems in atomizers for fuel applications where fuel lines and atomizers become plugged by tarry polymeric deposits.

(b) The water content is high, usually in the range of 15% to 30%, which decreases the specific heating value. On the other hand, this water is necessary to render the liquid fluid at low temperatures.

(c) The liquid contains significant amounts of acids, especially formic and acetic acids, which renders them corrosive and limits the choice of materials for storage vessels, [S. Czernik, op.cit.].

(d) Their viscosities are high thus creating problems with atomization and smooth combustion in fuel applications. Furthermore, filtration and distillation are difficult.

[0008] These problems have triggered intensive efforts to devise methods for upgrading pyrolysis liquids. Particular

attention has been focused on hydrotreating using conventional petroleum catalysts, for example, cobalt-molybdenum or nickel-molybdenum on alumina to produce essentially oxygen-free naphthas. These processes have been comprehensively reviewed by A.V. Bridgwater [Applied Catalysis A, 116 (1994) 5-47].

5 [0009] Since pyrolysis liquids typically contain between 30 to 50 wt% of oxygen, complete removal of oxygen requires a substantial consumption of hydrogen, estimated to be as much as 600 to 1000 L/kg of pyrolysis liquid, [W. Baldauf, et al., in Proceedings, 7th European Conference on Biomass for Energy and Environment, Agriculture and Industry]. This represents a major and prohibitive cost.

10 [0010] Further drawbacks include the high capital and operating costs associated with high pressure catalytic hydrotreating and the difficulty of avoiding plugging of feed lines on account of the aforementioned thermal instability of the pyrolysis liquids.

15 [0011] An alternative approach currently under investigation is the use of zeolite catalysts for cracking and reforming of the pyrolysis liquid to generate hydrocarbon products. However, in spite of intense effort over many years, the results to date have been rather poor, [A.V. Bridgwater, supra]. The fundamental problem appears to be the fact that zeolites, being acid catalysts, are therefore excellent dehydration agents while the hydrogen content of biomass pyrolysis liquids is close to what is stoichiometrically required to remove their oxygen content as water. Therefore, coking is a severe problem, hydrocarbons obtained are principally of undesirable aromatic character and even these are obtained in only low yields.

20 [0012] In a paper entitled, "Development of Methods for the Stabilization of Pyrolytic Oils" by M.B. Polk, et al., Report EPA-600/2-81-201, prepared for Municipal Environmental Research Lab, Cincinnati, Ohio, September, 1981, it was recognized that acetals and esters form in small quantity slowly over time in aged samples of pyrolysis oil from reactions with alcohol already present in the oil. Polk, et al. attempted to stabilize the pyrolysis oil by hydrogenation and no attempt was made to enhance the formation of the acetals and esters.

25 [0013] An object of this invention is to provide an economical method for improving the liquid products from the pyrolysis of lignocellulosic materials and other biomass for the purposes of their use as liquid fuels in boilers, turbines and internal combustion engines.

[0014] Another object of this invention is to provide a method for reducing the corrosivity of the said biomass pyrolysis oils to minimize problems with their storage and handling.

30 [0015] Yet another object of this invention is to provide a method for enhancing the chemical and thermal stability of the said pyrolysis oils so as to prevent aging and thus to avoid the consequent problems of viscosity increases with time and deposition in fuel lines.

[0016] A further object of this invention is to provide a method for enhancing the specific heating value of the said pyrolysis oils by chemical combination of these oils with a suitable alcohol and further by reducing the water content of the oils.

35 [0017] A method of upgrading liquid products freshly obtained from the pyrolysis of biomass to chemically and thermally stabilize said products, said method comprising:

- 40 (a) adding alcohol to liquid products obtained from a pyrolysis process;
 (b) mixing the alcohol and liquid products;
 (c) removing the water without removing alcohol, thereby increasing the specific heat value and lowering acidity and viscosity.

[0018] Figure 1 is a graph comparing the overall material balance initially after the ethanol is added and after the completion of the reaction.

45 [0019] As a further consequence of the methods described in this invention, the viscosity of the said pyrolysis oils are substantially reduced which facilitates the pumping and atomization of these oils in combustion apparatus and improves their filterability which could be relevant for removing cation contaminants.

50 [0020] This invention is based on the discovery that, under appropriate conditions, pyrolysis oils obtained in the manner described will chemically combine with substantial quantities of various alcohols and that compared with the original pyrolysis oil, this modified product is of lower acidity, contains reduced amounts of aldehydic groups, is of lower viscosity, contains less water and has a higher specific heating value. These enhancements are expected to minimize most of the problems associated with the use of these oils as fuels.

55 [0021] In the preferred embodiment, the alcohol combined is ethanol. In particular, it was found that when a hardwood pyrolysis oil was mixed at room temperature with an excess of ethanol, a small quantity of a mineral acid and a suitable dehydrating agent (for example, Molecular Sieve 3A), astonishingly up to 40 wt% of the alcohol on the basis of the organic fraction of the oil became chemically combined with the oil. The resulting mixture had the desirable properties previously outlined.

[0022] Furthermore, analysis of this product showed the presence of certain acetals, hemiacetals and esters and possibly ethers. It therefore seems probable that the type of chemical reactions taking place might include esterification

of carboxylic acid groups, acetalization of aldehyde groups and possibly ketalization of ketone groups. Furthermore, transacetalization and transesterification reactions are also likely to occur. Other possibilities include etherification of hydroxyl groups, though this seems unlikely under the mild conditions employed.

[0023] Accordingly, several pyrolysis liquids obtained by fluidized bed flash pyrolysis of different feedstocks at different temperatures were analysed for functional group content with the results shown in the following Table 2:

| Feedstock | Pyrolysis Temperature (°C) | Moles Functional Groups /kg Organic Liquid | | | | |
|--------------|----------------------------|--|----------|----------|----------|----------|
| | | Carboxyl | Carbonyl | Hydroxyl | Phenolic | Methoxyl |
| Maple | 480 | 2.1 | 5.7 | 0.92 | 2.8 | 2.1 |
| Wheat Straw | 500 | 1.4 | 5.3 | 1.40 | 3.0 | 1.1 |
| Poplar-Aspen | 450 | 2.1 | 6.2 | 0.77 | 2.8 | 1.6 |
| " | 500 | 1.6 | 6.9 | 0.87 | 2.8 | 1.5 |
| " | 550 | 1.7 | 6.6 | 0.77 | 2.8 | 1.2 |
| Peat Moss | 520 | 1.2 | 3.0 | 1.30 | 1.8 | 0.7 |

[0024] It was determined that in many instances, a large fraction of the carbonyl groups consist of only a few simple aldehydes, namely hydroxyacetaldehyde, glyoxal, methyl glyoxal, formaldehyde and acetaldehyde. This is significant since acetalization of aldehydes is a more facile process than ketalization of ketones. Similarly, only a few simple carboxylic acids, especially formic and acetic acids, appear to be the principal contributors to the carboxyl group content. Some typical concentrations of some of these compounds in biomass pyrolysates obtained by pyrolysis at around 500°C of a range of biomass feedstocks including wood, agricultural wastes, forest residues and industrial biomass wastes are shown in Table 3 below:

| Feedstock | Wt % of Organic Liquid Product | | | | | | |
|---------------------|--------------------------------|-------------|----------|--------------------|-----------------|-------------------------|-----------|
| | Poplar-Aspen Wood | Wheat Chaff | Hog Fuel | Bleached Cardboard | Sorghum Bagasse | Sulfite Pulp Mill waste | Peat Moss |
| Hydroxyacetaldehyde | 15.2 | 12.8 | 8.0 | 19.3 | 12.2 | 17.0 | 1.4 |
| Glyoxal | 3.3 | 1.4 | 1.1 | 2.6 | 0.6 | 1.4 | n.d. |
| Formaldehyde | 1.8 | 2.6 | 1.8 | 6.6 | 6.1 | n.d. | n.d. |
| Formic Acid | 4.7 | n.d. | 2.3 | n.d. | n.d. | 3.6 | 15.5 |
| Acetic Acid | 8.3 | 12.0 | 5.6 | n.d. | 4.3 | n.d. | 4.5 |
| "Pyrolytic Lignin" | 24.6 | 29.6 | 59.4 | 4.0 | 30.6 | 6.4 | 49.2 |

[0025] It is apparent that in the case of poplar wood, for instance, the simple aldehydes listed can contribute in excess of 50% of the carbonyl groups present while formic and acetic acids can constitute nearly all the carboxyl groups. Nevertheless, the identities of many of the carbonyl compounds remain unknown in most cases.

[0026] If indeed the principal reactions taking place are acetalization and esterification, then these results show that, depending on the feedstock, a total of between six and eleven moles of carboxyl, carbonyl and phenolic groups are available for reaction with alcohol. For instance, assuming that carbonyl and carboxyl groups are present in a 3:1 ratio and react completely with the alcohol and that phenols do not react, then reaction of a hardwood pyrolysate with ethanol would result in the incorporation of over 40 wt% of ethanol/kg of organic liquid product. This is in agreement with the maximum ethanol incorporation mentioned before and suggests that essentially all the carbonyl and carboxylic groups have reacted under the given conditions.

[0027] The following examples are intended to illustrate the various aspects of the present invention without limiting the invention in any way.

Example 1:

[0028] Sawdust, from Alberta poplar wood, was pyrolyzed in a fluidized bed and the vapours and aerosols condensed to produce a tar. This fresh tar was dissolved in a sufficient amount of ethanol so that the concentration of ethanol was 51.6 wt% as determined by gas chromatography. The initial water content of the mixture was 1.74 wt% as determined by Karl Fischer analysis which has been established as a reliable method for biomass pyrolysis liquids. The remainder of the sample (46.7 wt%) consisted of the organic fraction of the pyrolysis tar. Next, 1.4 wt% of sulfuric acid was added

as a catalyst to this solution.

[0029] Molecular Sieve 3A was used as a desiccant to remove water of reaction and thereby to drive any reversible reactions to completion. This sieve has a sufficiently small pore size that only water should be absorbed within the pores though adsorption of organic species may be expected to occur on the external surfaces. Fifteen grams of the activated molecular sieve were added to 40.6 g of the solution and the mixture was allowed to stand at room temperature. Within a few minutes, ester and acetal peaks began to appear in the gas chromatographic trace of the solution. After two hours, the solution was again analyzed quantitatively. In addition, the ethanol content was determined to be 35.9 wt% and the water content was 0.28 wt%. The gas chromatographic analysis also showed the presence of substantial amounts of ethyl acetate, acetyl formate and the diethoxyacetal of hydroxyacetaldehyde. In addition, there were several other new but unidentified peaks of volatile components. These results indicate that ethanol has been reacted to form at least esters and acetals and possibly ethers as well. The formation reactions for such compounds all liberate water. The reduced water content of the sample therefore implies that the molecular sieve was effective in removing both the water present initially as well as the water of reaction.

[0030] Since an unknown amount of water was absorbed by the molecular sieve, the actual mass of ethanol present cannot be directly calculated from its final concentration. However, on the basis of the results, it is possible to estimate the amount of ethanol reacted if some assumptions are made about the combined amount of water liberated in the acetalization and esterification reactions. Full acetalization yields 0.196 kg of water per kg of ethanol reacted while esterification yields 0.391 kg of water per kg of ethanol. In the absence of detailed knowledge of the relative proportions of these products in the final solution, it will be assumed that the average, 0.29kg/kg ethanol, of these two values is also the average amount of water liberated by the ethanol reacted. By applying the appropriate mass balance equations, it is then possible to estimate the final masses of free ethanol and of the organic fraction of the pyrolysis tar. These were found to be 13.5 g and 24.1 g respectively.

[0031] These results imply that there was chemical uptake by reaction of 0.394 kg of ethanol per kg of organic material originally present in the pyrolysis tar. This is astonishingly high, but is in excellent agreement with the estimate made in the previous section of the maximum possible level of incorporation of alcohol. The overall material balance is illustrated graphically in Figure 1.

[0032] It is possible to estimate the calorific value of the modified pyrolysis tar using the standard formula:

$$\text{Calorific value in MJ/kg} = 33 \times \text{mass fraction of Carbon} + 143 \times \text{mass fraction of Hydrogen}$$

[0033] Typically, the hardwood pyrolysis tars contain 52 wt% carbon and 6 wt% hydrogen on a moisture-free basis so the initial heating value is estimated to be 25.7 MJ/kg. On the other hand, it is possible to estimate the calorific value of the tar after chemical combination with ethanol by making use of the same assumptions made in calculating the mass balance. The result is that the final elemental composition on an ethanol and water-free basis is 57 wt% carbon and 7.7 wt% hydrogen giving an estimated calorific value of 29.7 MJ/kg, an increase of about 16%.

Example 2:

[0034] In this example, the reactivity of a fresh pyrolysis tar with respect to uptake of an alternative alcohol, methanol, was investigated. A sample of mixed hardwoods were pyrolyzed at 425°C and the tar collected was dissolved in methanol so that the initial concentration of methanol was 26.0 wt%. The water content of the solution was 5.99 wt% initially. Sulfuric acid of 1.5 wt% was added along with an amount of activated Molecular Sieve 3A equivalent to 75% of the total weight of the solution. The sample was allowed to stand for two hours at room temperature and was then analyzed. The final methanol concentration was only 24.22 wt%, indicating a relatively low level of reaction with the pyrolysis tar. The final water content was 0.2 wt%.

[0035] The extent of chemical combination of methanol with the organic fraction of the pyrolysate can be estimated using the calculational scheme outlined in Example 1. The result is that the uptake was only 0.0533 kg of methanol/kg of organic material originally present in the pyrolysis tar. This is much less than that obtained with ethanol in Example 1.

Example 3:

[0036] In this example, a mixture of two alcohols was tested. The hardwood pyrolysate used in Example 3 was dissolved in a mixture of methanol and n-propanol so that the initial concentrations of the alcohols were 18.72 and 28.01 wt% respectively. The initial water content of this mixture was 4.31 wt% and the mass fraction of organics from the pyrolytic tar amounted to 48.96 wt% of it. To this solution was added 3.34 wt% sulfuric acid as catalyst and the whole mixture placed over an amount of Molecular Sieve 3A equivalent to 80 wt% of it.

[0037] After five hours on standing at room temperature, the mixture was analyzed and found to contain 12.32 wt% and 17.76 wt% of methanol and n-propanol respectively. The final water concentration was small (less than 0.2 wt%). Applying mass balances for the organic fraction, as well as for the two alcohols in the manner outlined in Example 1, enables a determination of the uptake of the individual alcohols. These were found to be 0.134 kg methanol and 0.214 kg n-propanol per kg of organic material originally present in the pyrolysis tar. The total alcohol uptake was therefore comparable to that obtained with ethanol in Example 1.

Example 4:

[0038] In this example, an attempt was made to combine ethanol with an aged sample of a pyrolytic tar obtained by flash pyrolysis of Eucalyptus wood. This tar contained a high proportion of pyrolytic lignin (36.4 wt% of the organic fraction of the liquid) with a correspondingly low concentration of low molecular weight carbonyl compounds. For example, hydroxyacetaldehyde was only 7.1 wt% of the organic fraction of the tar. Furthermore, hydrochloric acid was used as an alternative catalyst for the reaction.

[0039] Equal masses of the tar and ethanol were combined. The initial overall water concentration of mixture was 11.90 wt%. Concentrated hydrochloric acid of 4.2 wt% was added to the mixture along with a mass of Molecular Sieve 3A equal to the total mass to the mixture. After standing at room temperature for five hours, the water content was reduced to 0.05 wt% and the ethanol content was reduced to 48.0 wt%. Estimation of the ethanol consumption, by means of the material balance procedure outlined in Example 1, showed that 0.158 kg ethanol per kg of organic material in the tar had reacted. This value, which is significantly lower than that obtained in Example 1, is consistent with the relatively high lignin content and relatively low concentrations of acids and aldehydes in the tar initially. This example also demonstrates that uptake of alcohol can be achieved with different acid catalysts.

[0040] These examples are intended solely to illustrate the results that can be achieved and are not intended to restrict in any way the precise details by which the reactions may be carried out. Thus, it would be expected that in practice, the process would be carried out on a continuous basis with the mixture of pyrolytic tar and alcohol pumped through a column of molecular sieve. Alternatively, it might be more efficacious to combine the pyrolytic tar with sufficient ethanol to ensure a low initial concentration of water then to distill off the excess ethanol, which would cause water to be removed azeotropically and then to dry the ethanol over molecular sieve or by some other means. Yet another alternative would be to remove water continuously during the reaction by azeotropic distillation with an immiscible solvent. If sulfuric acid is used as a catalyst, it can be removed from the final mixture by adding lime and filtering off the precipitated calcium sulfate. Alternatively, a solid acid catalyst may be employed in which case this step would be unnecessary.

[0041] The chemical reactions described herein are believed to occur. However, the actual chemical reactions may be different from those described herein without affecting the manner in which the method can be carried out. Variations within the scope of the attached claims will be readily apparent to those skilled in the art.

[0042] It might also be deemed desirable to separate some of the specific products obtained by the process for use in other applications. For example, the esters of acetic and formic acids are known commercial chemicals, while the acetals of hydroxyacetaldehyde and glyoxal may have value as solvents, fuel additives or as flavour chemicals.

Claims

1. A method for upgrading liquid products obtained from the pyrolysis of biomass for use as at least one of chemical feedstocks and fuel, said method comprising:
 - (a) adding alcohol to said liquid products obtained from a pyrolysis process;
 - (b) chemically reacting the alcohol with said liquid products using an acid catalyst;
 - (c) removing water thereby driving the reaction to completion.
2. A method as claimed in Claim 1 including the steps of adding an amount of alcohol that is selected from the group consisting of stoichiometric, sub-stoichiometric and excess.
3. A method as claimed in any one of Claims 1 or 2 wherein the method is carried out using ethanol as the alcohol.
4. A method as claimed in Claim 1 including the steps of adding an excess of ethanol, a small quantity of mineral acid as a catalyst and a suitable dehydrating agent to the liquid products of pyrolysis.
5. A method as claimed in Claim 4 wherein the dehydrating agent is a molecular sieve used to separate water from

the liquid products.

6. A method as claimed in Claim 5 including the step of using Molecular Sieve 3A as the molecular sieve.
- 5 7. A method as claimed in any one of Claims 4, 5 or 6 wherein the mineral acid is sulphuric acid.
8. A method as claimed in any one of Claims 1, 2 or 3 including the steps of converting any aldehydic, ketonic and carboxylic compounds present to acetals, ketals and esters, respectively.
- 10 9. A method as claimed in any one of Claims 1, 2 or 3 including the steps of carrying out the method on a continuous basis.
10. A method as claimed in any one of Claims 1, 2 or 3 including the steps of carrying out the method on a continuous basis by pumping a mixture of said liquid products and alcohol through a column of a molecular sieve.
- 15 11. A method as claimed in any one of Claims 1, 2 or 3 including the steps of combining the liquid products with sufficient ethanol to ensure a low initial concentration of water, distilling off the excess ethanol and subsequently drying the ethanol.
- 20 12. A method as claimed in any one of Claims 1, 2 or 3 including the steps of removing water continuously during the reaction by azeotropic distillation with an immiscible solvent.
13. A method as claimed in any one of Claims 3, 4 or 5 including the steps of removing the mineral acid from the final mixture by adding lime and filtering off the precipitated calcium salt.
- 25 14. A method as claimed in any one of Claims 1, 2 or 3 including the step of using a solid acid catalyst as the mineral acid.
15. A fuel obtained by chemically reacting pyrolysis oil and alcohol.
- 30 16. A chemical feedstock obtained by chemically reacting pyrolysis oil and alcohol.

Patentansprüche

- 35 1. Verfahren zum Aufarbeiten von flüssigen Produkten, die aus der Pyrolyse von Biomasse erhalten werden, zur Verwendung als zumindest ein Stoff für chemische Ausgangsstoffe und als Brennstoff, wobei das Verfahren umfaßt:
- 40 (a) das Zusetzen eines Alkohols zu den flüssigen Produkten, die aus einem Pyrolyseverfahren erhalten werden;
- (b) das chemische Reagieren des Alkohols mit den flüssigen Produkten unter Verwendung eines sauren Katalysators;
- 45 (c) das Entfernen von Wasser, wodurch die Reaktion zum Abschluß gebracht wird.
2. Verfahren nach Anspruch 1, wobei es den Schritt des Zusetzens von Alkohol in einer Menge umfaßt, die aus der Gruppe ausgewählt ist, die stöchiometrisch, unterstöchiometrisch und überschüssig zusammengesetzt ist.
3. Verfahren nach Anspruch 1 oder 2, wobei das Verfahren unter Verwendung von Ethanol als Alkohol ausgeführt wird.
- 50 4. Verfahren nach Anspruch 1, wobei das Verfahren die Schritte des Zusetzens eines Überschusses an Ethanol, einer kleinen Menge Mineralsäure als Katalysator und eines geeigneten Dehydrationsmittels zu den flüssigen Produkten der Pyrolyse umfaßt.
- 55 5. Verfahren nach Anspruch 4, wobei das Dehydrationsmittel ein Molekularsieb ist, das zur Abtrennung von Wasser aus den flüssigen Produkten verwendet wird.

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6. Verfahren nach Anspruch 5, wobei es den Schritt des Verwendens des Molekularsiebes 3A als Molekularsieb umfaßt.
- 5 7. Verfahren nach einem der Ansprüche 4, 5 oder 6, wobei die Mineralsäure Schwefelsäure ist.
8. Verfahren nach einem der Ansprüche 1, 2 oder 3, wobei es den Schritt der Umwandlung jeglicher vorhandener Aldehyd-, Keton- und Carbonsäureverbindungen entsprechend zu Acetalen, Ketalen und Ester umfaßt.
- 10 9. Verfahren nach einem der Ansprüche 1, 2 oder 3, wobei es den Schritt der kontinuierlichen Ausführung des Verfahrens umfaßt.
10. Verfahren nach einem der Ansprüche 1, 2 oder 3, wobei es den Schritt der kontinuierlichen Ausführung des Verfahrens durch Pumpen einer Mischung der flüssigen Produkte und Alkohol durch eine Säule mit einem Molekularsieb umfaßt.
- 15 11. Verfahren nach einem der Ansprüche 1, 2 oder 3, wobei es die Schritte umfaßt, die flüssigen Produkte mit ausreichend Ethanol zu mischen, um eine geringe Anfangskonzentration mit Wasser sicherzustellen, das überschüssige Ethanol abzudestillieren und das Ethanol anschließend zu trocknen.
- 20 12. Verfahren nach einem der Ansprüche 1, 2 oder 3, wobei es den Schritt des kontinuierlichen Entfernens von Wasser während der Reaktion durch azeotrope Destillation mit einem nicht mischbaren Lösemittel umfaßt.
13. Verfahren nach einem der Ansprüche 3, 4 oder 5, wobei es die Schritte des Entfernens der Mineralsäure aus der letztlich vorliegenden Mischung durch Zugeben von Kalk und des Abfiltrierens des ausgefallenen Kalziumsalzes umfaßt.
- 25 14. Verfahren nach einem der Ansprüche 1, 2 oder 3, wobei es den Schritt des Verwendens eines festen sauren Katalysators als Mineralsäure umfaßt.
- 30 15. Brennstoff, der durch chemische Reaktion von Pyrolyseöl und Alkohol erhalten wird.
16. Chemischer Ausgangsstoff, der durch chemische Reaktion von Pyrolyseöl und Alkohol erhalten wird.

35 **Revendications**

1. Procédé pour améliorer des produits liquides obtenus à partir de la pyrolyse de biomasse pour être utilisés en tant que produits chimiques de base et/ou carburants, ledit procédé comprenant :
- 40 (a) ajouter de l'alcool auxdits produits liquides obtenus à partir d'un processus de pyrolyse ;
(b) faire réagir chimiquement l'alcool avec lesdits produits liquides en utilisant un catalyseur acide ;
(c) retirer l'eau conduisant ainsi la réaction jusqu'à sa fin.
2. Procédé selon la revendication 1, comprenant les étapes d'ajouter une quantité d'alcool qui est choisi à partir du groupe constitué de quantités stœchiométrique, substoichométrique et en excès.
- 45 3. Procédé selon l'une des revendications 1 ou 2, dans lequel le procédé est réalisé en utilisant de l'éthanol en tant qu'alcool.
- 50 4. Procédé selon la revendication 1, comprenant les étapes d'ajouter un excès d'éthanol, une petite quantité d'acide minéral en tant que catalyseur et un agent déshydratant approprié aux produits liquides de pyrolyse.
5. Procédé selon la revendication 4, dans lequel l'agent déshydratant est un tamis moléculaire utilisé pour séparer l'eau des produits liquides.
- 55 6. Procédé selon la revendication 5, comprenant l'étape d'utiliser un Tamis Moléculaire A3 en tant que tamis moléculaire.

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7. Procédé selon l'une quelconque des revendications 4, 5 ou 6, dans lequel l'acide minéral est de l'acide sulfurique.
8. Procédé selon l'une quelconque des revendications 1, 2 ou 3, comprenant les étapes de convertir tout composé aldéhydique, cétonique et carboxylique présents en acétales, cétales et esthers respectivement.
- 5 9. Procédé selon l'une quelconque des revendications 1, 2 ou 3, comprenant l'étape de mettre en oeuvre le procédé sur une base continue.
- 10 10. Procédé selon l'une quelconque des revendications 1, 2 ou 3, comprenant l'étape de mettre en oeuvre le procédé sur une base continue en pompant un mélange desdits produits liquides et de l'alcool à travers une colonne d'un tamis moléculaire.
- 15 11. Procédé selon l'une quelconque des revendications 1, 2 ou 3, comprenant les étapes de combiner les produits liquides avec suffisamment d'éthanol pour assurer une faible concentration initiale en eau, de distiller l'excès d'éthanol et d'assécher ensuite l'éthanol.
- 20 12. Procédé selon l'une quelconque des revendications 1, 2 ou 3, comprenant les étapes de retirer l'eau continuellement pendant la réaction par distillation azéotropique avec un solvant immiscible.
- 25 13. Procédé selon l'une quelconque des revendications 3, 4 ou 5, comprenant les étapes de retirer l'acide minéral du mélange final en ajoutant de la chaux et de filtrer le sel de calcium précipité.
- 30 14. Procédé selon l'une quelconque des revendications 1, 2 ou 3, comprenant l'étape d'utiliser un catalyseur acide solide en tant qu'acide minéral.
- 35 15. Carburant obtenu en faisant réagir chimiquement de l'huile de pyrolyse et de l'alcool.
- 40 16. Produit chimique de base obtenu en faisant réagir chimiquement de l'huile de pyrolyse et de l'alcool.
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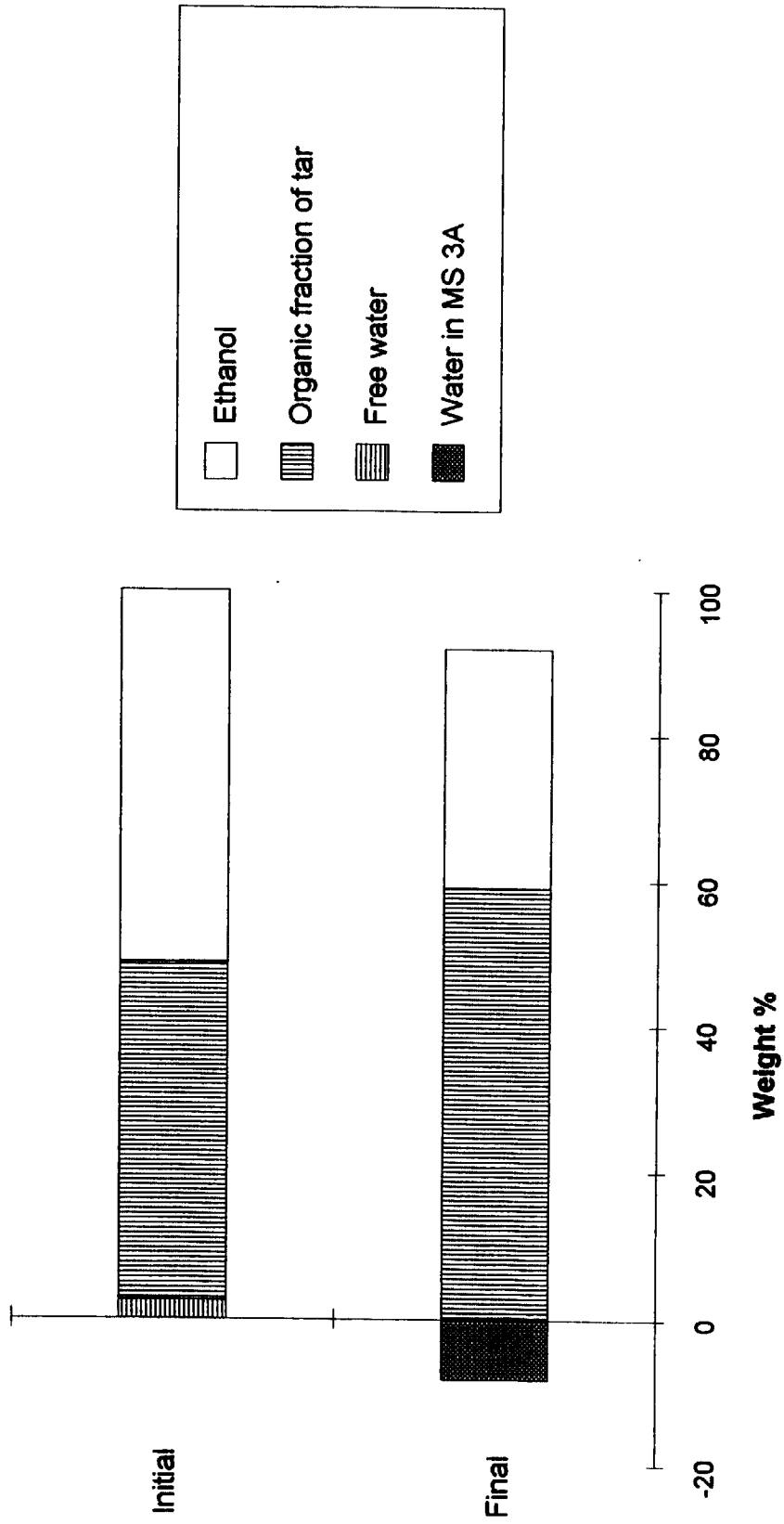


Figure 1