



(51) International Patent Classification:

C10G 1/00 (2006.01)

C10B 53/02 (2006.01)

C10G 1/02 (2006.01)

C10G 45/44 (2006.01)

C10G 1/08 (2006.01)

C10G 45/46 (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/NL2017/050419

(22) International Filing Date:

23 June 2017 (23.06.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2017044

24 June 2016 (24.06.2016)

NL

(71) Applicant: BIOBTX B.V. [NL/NL]; De Mudden 14, 9747 AW Groningen (NL).

(72) Inventors: HEERES, André; c/o De Mudden 14, 9747 AW Groningen (NL). SCHENK, Niels Jan; c/o De Mudden 14, 9747 AW Groningen (NL). KRUIZE-MUIZE-BELT, Inouk; c/o De Mudden 14, 9747 AW Groningen (NL).

(74) Agent: JANSEN, C.M.; V.O., Carnegieplein 5, 2517 KJ Den Haag (NL).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: PROCESS FOR THE PREPARATION OF LOW MOLECULAR WEIGHT AROMATICS (BTX) AND BIOFUELS FROM BIOMASS

(57) Abstract: A process for the preparation of aromatic compounds from a feed stream containing biomass or mixtures of biomass, the process comprising: a) subjecting a feed stream containing biomass or mixtures of biomass to a process to afford a conversion product comprising aromatic compounds; b) recovering the aromatic compounds from said conversion product; c) separating a higher molecular weight fraction comprising polyaromatic hydrocarbons (PAH) from a lower molecular weight fraction comprising benzene, toluene and xylene (BTX) by distillation; d) reducing at least part of said higher molecular weight fraction to obtain a reduced fraction comprising polycyclic aliphatics (PCA); and e) subjecting the higher molecular weight fraction obtained in step c), the reduced fraction obtained in step d), or a mixture thereof, to a process to obtain lower molecular weight aromatics (BTX).



Title: Process for the preparation of low molecular weight aromatics (BTX) and biofuels from biomass.

5

The present invention relates to a novel process for the preparation of benzene, toluene and xylenes (BTX) and a biofuel containing higher aromatics from a feed stream comprising biomass or mixtures of biomass. It also relates to unique compositions obtainable thereby, and to the use of such compositions.

10

Low molecular weight monocyclic aromatic compounds such as benzene, toluene, and xylenes are important starting materials for a large number of applications. Benzene is an intermediate in, e.g., in the production of ethylbenzene, cumene, cyclohexane and adipic acid. Toluene is an intermediate for e.g., toluenediisocyanate, benzaldehyde and benzoic acid and has also found application as a solvent, e.g. for paints, printing ink and glues. From the three isomers of xylene p-xylene is often used in the preparation of para-terephthalic acid, a monomer for the preparation of several polyesters and polyamides. o-Xylene is mainly used in the production of plasticizers for PVC, m-xylene is most often converted to isophthalic acid and subsequently used in co-polymerizations with p-terephthalic acid and 3,3',4,4'-tetraaminodiphenyl.

20

Currently, the above-described aromatic compounds are produced via refinery processes of fossil fuels. Common processes include steam cracking, steam reforming and catalytic reforming. In order to achieve a more environmentally friendly and sustainable route, independent from the oil production, lots of academic and industrial groups focused on routes towards BTX from biomass and mixtures thereof. From the current routes described especially catalytic pyrolysis is attractive, owing to a one-step procedure and high flexibility in biomass input. Various patents and articles in the open literature describe the conversion of different biomass streams and mixtures thereof with most often zeolite-based catalysts using direct catalytic pyrolysis. In this approach the catalyst is mixed with the biomass, or an *ex situ* upgrading process is used in which the biomass is first (catalytically) pyrolyzed and the vapors obtained are subsequently *ex situ* aromatized with most often specific zeolite catalysts. In all cases a mixture of

25

30

aromatics is obtained consisting of alkyl substituted mono-, bi, tri and tetracyclic aromatics. The amount of the more valuable BTX in this mixture of aromatics is dependent on process conditions and the biomass used, but most often it is the minority of the total aromatics formed. As a result, there is a strong demand for a commercially attractive process converting biomass, or mixtures thereof, in high yields towards the more valuable compounds benzene, toluene and xylenes (BTX).

It was surprisingly found that a unique high molecular weight fraction comprising polyaromatic hydrocarbons (PAH), polycyclic aliphatics (PCA), mono-aromatic polycyclic hydrocarbons (MPH) , or mixtures thereof, can be isolated during and/or after the biomass conversion process, and that the co-feeding of said fraction with a biomass feedstream greatly increases the yield of BTX.

Accordingly, in one aspect the present invention provides a process for the preparation of aromatic compounds from a feed stream containing biomass or mixtures of biomass, the process comprising:

a) subjecting the biomass feed stream to a process to afford a conversion product comprising aromatic compounds; b) recovering the aromatic compounds from said conversion product; c) separating a higher molecular weight fraction comprising polyaromatic hydrocarbons (PAH) from a lower molecular weight fraction comprising benzene, toluene and xylene (BTX) by distillation; d) reducing at least part of said higher molecular weight fraction to obtain a reduced fraction comprising polycyclic aliphatics (PCA); and e) subjecting the higher molecular weight fraction obtained in step c), the reduced fraction obtained in step d), or a mixture thereof, to a process to obtain lower molecular weight aromatics (e.g. BTX).

In one embodiment step a) of a process according to the invention comprises subjecting the biomass feed stream to *in situ* or *ex situ* pyrolysis, or to a vaporization process. Preferably, subjecting the biomass feed stream to a process to afford a conversion product comprises pyrolysis of the biomass feed, preferably using a cheap cracking catalyst, followed by subsequently subjecting the vapors thus obtained to an *ex situ* catalytic aromatization step.

In step b), the aromatic compounds are recovered from the conversion product of step a), after which in step c) a unique higher molecular weight fraction comprising polyaromatic hydrocarbons (PAH) is separated from a lower molecular weight fraction comprising benzene, toluene and xylene (BTX) by distillation.

5

As will be described herein below, the polyaromatic hydrocarbon fraction, obtained after the distillation of BTX, can subsequently be (re)-utilized in the pyrolysis, thereby affording a mixture of BTX and higher aromatics. More in particular, at least part of the polyaromatic fraction obtained after distillation of BTX is first
10 reduced (e.g., by catalytic hydrogenation) in step d) towards polycyclic aliphatics (PCA), polyaromatic hydrocarbons (PAH), mono-aromatic polycyclic hydrocarbons (MPH, e.g. substituted tetralins) or a mixture of PCA, PHA and/or MPH, preferably PCA/PAH, and thereafter (re)-utilized in the pyrolysis.

In step e) the higher molecular weight fraction obtained in step c), the reduced
15 fraction obtained in step d), or a mixture thereof, is subjected to a process to obtain lower molecular weight aromatics (e.g. BTX).

In one embodiment, the above described high molecular weight fractions (partially or fully reduced or not) are co-fed with a biomass or mixtures thereof, thereby
20 resulting in significant higher yields of BTX. The BTX can easily be distilled and the remaining higher aromatic fraction can again be utilized in the pyrolysis or, alternatively, first reduced to an aliphatic/aromatic fraction and re-utilized in the pyrolysis step. The above-described process is depicted in Figures 1 and 2.

Repeating the above-described procedure will result in high conversions of biomass
25 towards BTX.

Figures 3 and 4 show, respectively, the ^1H -NMR spectra of the polyaromatic fraction and the ^1H -NMR of the reduced fraction, obtained by catalytic hydrogenation. It clearly shows that the amount of aromatic protons present between 6.5-8.0 ppm are less in intensity and mostly converted to aliphatic
30 hydrocarbons. The conversion of the polyaromatic fraction towards aliphatics is confirmed by GC analysis (see Figure 5) and Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) measurements (Figures 6 and 7).

In the present invention, the initial aromatic fraction in step a) may be obtained via catalytic pyrolysis of hydrocarbonaceous material. It will be understood that the composition of the vaporous fraction to some extent depends on the nature of the feed stream and the conditions applied. It has been found that good results are
5 obtained with feed streams comprising biomass selected from the group consisting of agricultural waste, plants, wood, and combinations thereof. The feed stream suitably comprises organic material such as, glucose, maltose, starch, cellobiose, cellulose, hemi-cellulose, other polysaccharides, lignin, sugar cane bagasse, lignocellulosic materials (e.g., wood chips or shavings, lignocellulosic biomass, etc.),
10 glycerol, fatty acids, fatty acid methyl esters, triglycerides, food waste, animal waste, manure and corn stover. Also partially decayed vegetation, such as peat or even lignite can be used as biomass feed material in the process of the present invention. The feed stream preferably comprises crude glycerol and/or triglycerides

The resulting aromatic fraction from the above-described feed streams can
15 be separated from aqueous condensables, as phase separation occurs. After distillation of BTX, the higher substituted aromatics fraction can be re-utilized in the pyrolysis step or subsequently be reduced to a polycyclic alkanes or mixtures of polycyclic alkanes /polyaromatic hydrocarbon/mono-aromatic polycyclic hydrocarbons. The hydrogenation can be complete, resulting in a fraction
20 consisting of polycyclic aliphatics (PCA). Typically, it is not complete in the sense that not all polyaromatic molecules are reduced and/or in that not all aromatic rings of a single polyaromatic molecule are reduced. In that case, the reduced fraction may comprise, in addition to polycyclic aliphatics (PCA), also polyaromatic hydrocarbons (PAH) and/or mono-aromatic polycyclic hydrocarbons (MPH, e.g.
25 substituted tetralins). This mixture can be catalytically pyrolyzed towards BTX/aromatics or co-fed with the above-described feed streams in order to produce BTX/aromatics.

In the present invention the aromatics can be formed by a pyrolysis reaction of biomass with a catalyst, a pyrolysis of a mix of biomass with a polyaromatic
30 hydrocarbon fraction and a catalyst, a mixed polycyclic alkanes/polyaromatic hydrocarbon fraction or a polycyclic alkane fraction and a catalyst. It is well known that a variety of pyrolysis techniques are able to produce such a fraction from biomass feed (G.W. Huber, S. Iborra, A. Corma, Chem. Rev., 2006, 4044-4098). A

particularly desirable form is catalytic fast pyrolysis and this involves the rapid heating of a biomass feed stream under an inert atmosphere in the presence of a catalyst (A.V. Bridgwater, *Cat Today*, 1996, 285-295; A.J. Forster, J. Jae, Y.T. Ching, G.W. Huber, R.F. Lobo, *Appl. Cat. A: General.*, 2012, 154-161 and G.W. Huber, H. Zhang, T. Carlson, WO2013/032672). The pyrolysis can be performed *in situ*, in which the catalyst is mixed with the biomass and pyrolysed thereafter or, alternatively, *ex-situ* in which the biomass is non-catalytically pyrolyzed and in a second reactor catalytically transformed towards a mixture of aromatics. Within our invention the biomass can be co-fed with the polyaromatic hydrocarbon fraction or the polycyclic alkanes/polyaromatic hydrocarbon/ mono-aromatic polycyclic hydrocarbon fraction in order to increase the amount of BTX.

In a highly preferred embodiment, a method is used in which a cheap cracking catalyst is utilized in the pyrolysis step, followed by an *ex situ* catalytic aromatization step (Integrated Cascading Catalytic Pyrolysis). The latter method has the advantage that the aromatization catalyst will not be contaminated with inorganic material present in biomass and the cheap cracking catalyst influences both the yield and the composition of the vaporous fraction and allows thus the skilled person to produce significantly higher amounts of aromatics in the subsequent aromatization step (Figure 8; see also WO 2015/047085 A1). Within our invention the biomass can also in this case be co-fed with the polyaromatic hydrocarbon fraction or the polycyclic alkanes/polyaromatic hydrocarbon fraction in order to increase the amount of BTX.

Referring to Figure 8, a feed stream containing biomass, or a mixture of biomass, mixtures of biomass, or a mixture of biomass and a polycyclic alkanes/polyaromatic fraction or a polycyclic alkanes/polyaromatic fraction/mono-aromatic polycyclic hydrocarbons or a polycyclic alkane fraction is passed into a pyrolysis reactor A. To the reactor A also a stream of cracking catalyst is passed via a line 2. In the pyrolysis reactor A the cracking catalyst and feed stream are contacted with each other at pyrolysis conditions to yield a vaporous phase and a solid phase which consists of the cracking catalyst with coke residues deposited thereon. After the reaction the vaporous fraction is passed via a line 3 to reactor B. The coke-laden cracking catalyst may be recycled to the reactor A. It may also be

subjected to regeneration by burning off of the coke from the cracking catalyst. It may also be used as landfill, e.g. after removal of the coke.

In reactor B the vapor phase from reactor A is converted by a catalyst into aromatic compounds. The conversion product leaves the reactor B as a vapor via a line 7. Although reactor B has been depicted as a fixed-bed reactor it is emphasized that also a moving bed reactor, fluid bed reactor, or circulating fluid bed reactor is feasible. In either case zeolitic aromatization catalyst may be removed from the reactor B. The conversion product is subsequently passed into an extraction column C where it is contacted with a liquid hydrocarbon stream that is sprayed into the column C via a line 8 that is provided with a nozzle or manifold. Due to the contact with the liquid hydrocarbon, the aromatic compounds in the conversion product condense and are withdrawn, together with other liquids, e.g. liquid oxygen-containing compounds, via a line 10. Any residual gases are discharged via a line 9 for further treatment and disposal (not shown). The liquid aromatic products, liquid hydrocarbon and liquid oxygen-containing compounds in the line 10 are separated from each other, e.g. by phase extraction and/or fractionation (not shown). The BTX part of the aromatic fraction is distilled and, if preferred, the remaining higher aromatics reduced (partly) to polycyclic alkanes and re-utilized as co-feeding for reactor A.

The pyrolysis treatment of the feedstock may be carried out in a variety of reactors. Such reactors include a continuous stirred tank reactor (CSTR), a fixed bed reactor, a moving bed reactor, an auger reactor, a screw conveyor reactor, an entrained flow reactor, a rotating cone reactor and a fluidized bed reactor. Since the cracking catalyst tends to receive deposits of coke and other carbon residues it is preferred to employ a reactor that allows easy, and preferably continuous, regeneration. Therefore, the use of a CSTR, moving bed, an auger reactor, a screw conveyor reactor, an entrained flow reactor, a rotating cone reactor or fluidized bed reactor is preferred over the use of a fixed-bed reactor. Reactors that allow for a relatively short contact time and for intense mixing of the components of the feed stream with the cracking catalyst and for a continuous recirculation of regenerated catalyst to the pyrolysis zone are most preferred. Since this is the case for an auger reactor and a fluidized bed reactor, these reactors are particularly preferred.

Preferably, the aromatization catalyst is a zeolitic catalyst, suitably selected from aluminosilicates, SAPOs, silicalites and combinations thereof. It has been found that the second, aromatization catalyst preferably is acidic. The acidity may be influenced by the structure of the aluminosilicate and also by the ratio between
5 silicate moieties and aluminate moieties in the aluminosilicate. The acidity may e.g. be accomplished by ion exchange of the second, aromatization catalyst with ammonium salts and subsequent calcination thereof. The silica-alumina ratio (SAR) is relevant for the potential acidity of the second catalyst. At a low SAR and if virtually all the active sites have been rendered in the H^+ form, the resulting
10 catalyst is very acidic. It will be evident that the acidic sites on the aluminosilicates and the variation in SAR will enable the skilled person to determine what catalyst performs optimally for the relevant feed streams, reaction conditions and product slate. Suitable SARs include those in the range of 5 to 100, preferably, from 10 to 80, more preferably from 20 to 60. Another feature that may play a role in the
15 performance of the present catalyst is the pore diameter. It has been found that particularly good results are obtained if the pore diameter of the catalysts is in the range of 4.5 to 6.5 Å, preferably from 5 to 6 Å. Although the second catalyst may be a SAPO, the second catalyst is preferably a zeolite, that is selected from the group consisting of ZSM-5, ZSM-11, ZSM-35, ZSM-23, ferrierite, zeolite beta, zeolite Y,
20 zeolite X, mordenite, zeolite A, IM-5, SSZ-20, SSZ-55, MCM-22, TNU-9 and combinations thereof. In a preferred embodiment, use is made of a zeolite catalyst which has been impregnated with metals such as Ga and Zn in order to increase the yield of BTX. Combinations of catalysts can be mixed homogeneously or layered. It is not restricted to combinations of zeolite catalysts but also
25 combinations of a zeolite catalysts with e.g. a cracking catalysts are encompassed.

As indicated above, the acidity of the second, aromatization catalyst plays a role in the conversion of the vaporous fraction. The acidity may be related to the silica alumina ratio of the catalyst when the second, aromatization catalyst is a zeolitic catalyst. When the catalyst is a zeolitic catalyst also the pore size of the
30 zeolite catalyst is a factor in the process according to the present invention. Preferred pore diameters are those above. A preferred catalyst comprises a H-ZSM-5 zeolite with a silica-alumina ratio in the range of 15 to 100, preferably of about 20-60, since such H-ZSM-5 is most optimal for production of aromatics.

The conversion treatment is suitably carried out at a temperature in the range of 300 to 1000 °C. Relatively high temperatures, such as 450 to 650 °C are preferred since they tend to increase the formation of aromatic compounds from the vaporous phase. The pressure suitably ranges from 1 to 4 bar. In the conversion
5 treatment the catalyst is suitably present in a weight ratio of feed to catalyst in the range of 1:1 to 1:20.

Another preferred method for increasing the yield on aromatic compounds is constituted by the addition of one or more further reactants to the conversion treatment in step a) of a process of the invention. Such further reactant(s) can
10 suitably be selected from the groups consisting of extra olefins, alcohols, aldehydes, ketones, acids and combinations thereof. The further reactant suitably comprises from 1 to 6 carbon atoms. Examples of suitable further reactants include hydrogen, ethene, propene, butene, isobutene, pentenes and hexenes, methanol, ethanol, propanol or isopropanol and hexanol, formaldehyde and acetaldehyde, acetone,
15 methyl ethyl ketone, formic acid and acetic acid.

The vaporous phase, obtained after the aromatization process, is condensed to separate the extraction products into a gaseous and liquid fraction. The condenser may be a series of condensers well known in the art, but a suitable method for recovering the aromatic compounds from the conversion product is
20 constituted by a method wherein the conversion product is passed into an extraction column. A liquid hydrocarbon is sprayed into the conversion product thereby cooling the conversion product and providing a solvent for the aromatic compounds. Oxygen-containing compounds, including water that may be formed during the process, easily separate from the mixture of conversion product and
25 liquid hydrocarbon. In this way the aromatic hydrocarbons are recovered together with the liquid hydrocarbon.

The liquid phase is separated in an aqueous phase and an organic phase, containing the apolar aromatics. The organic fraction is subsequently distilled under atmospheric or slightly reduced pressure to distill off the high value
30 aromatics benzene, toluene, xylenes and ethylbenzene. The remaining polyaromatic hydrocarbon fraction consist of highly substituted single and multiple aromatic rings aromatics (C9 - ~C20) with an molecular weight between about 120 – 500D. For some embodiments this polyaromatic fraction is used as a biofuel or

utilized as an additive for conventional fuels. In another embodiment, the polyaromatic hydrocarbon obtained could be used as the spraying solvent in condensing the vaporous phases obtained in the catalytic aromatization process.

5 Step d) of a process herein disclosed comprises reducing at least part of said higher molecular weight fraction to obtain a reduced fraction comprising polycyclic aliphatics (PCA). For example, the above-described polyaromatic hydrocarbon fraction can easily be converted to a mixture of polycyclic and polyaromatic hydrocarbons by reduction. For example, liquid phase catalytic hydrogenation
10 affords, depending on the reaction conditions, a mixture of substituted aliphatic cycloalkanes/aromatic hydrocarbons. Suitable catalytic systems and reaction conditions to achieve the desired conversion are described in the open literature (A. Stanislaus, B.H. Cooper, Catal. Rev. Sci. Eng., 1994, 75-123). Accordingly, in a preferred aspect, step d) comprises catalytic hydrogenation, preferably using a
15 catalyst selected from the group consisting of Ru/C, Ni/C, Pd/C, Pt/C, MoS₂, WS₂, Co-Mo-S/Al₂O₃, Ni-Mo-S/Al₂O₃, Ni-W-S/Al₂O₃, Co-Mo/Al₂O₃ or homogeneous catalysts such as the Wilkinson catalyst and the Crabtree catalyst.

Preferably, the catalytic hydrogenation is performed without the addition of any other solvent. Owing to the robust ring strain, low freezing points and high
20 heat of combustions this fraction can be utilized as high-value biofuel for e.g., jet fuels.

In another embodiment, a selective catalytic hydrogenation towards mono-aromatic polycyclic alkanes is performed (Y. Cheng et al. Green Chem. (2009) 11, 1061-0165 and Y. Chen et al. Chem Cat Chem., (2015) 7, 978-998).

25

In step e) of a process according to the invention, the higher molecular weight fraction obtained in step c), the reduced fraction obtained in step d), or a mixture thereof, is subjected to a process for obtaining lower molecular weight aromatics (BTX). In one embodiment, step e) comprises mixing the higher molecular weight
30 fraction obtained in step c), the reduced fraction obtained in step d), or a mixture thereof, with a biomass feedstream and subjecting the resulting mixture to pyrolysis or vaporisation. Preferably, the process of step e) to obtain lower

molecular weight aromatics comprises a catalytic pyrolysis treatment. In a specific aspect, a process of the invention mixing the higher molecular weight fraction obtained in step c), the reduced fraction obtained in step d), or a mixture thereof, with the biomass feedstream of step a), thus yielding a recycling process.

5

Further aspects of the invention relate to unique compositions obtainable by some or all of the method steps of a process herein disclosed, and to the uses of such compositions. In one embodiment, the invention provides a composition comprising higher molecular weight polyaromatic hydrocarbons (PAH) obtainable by steps a) through c) of a method described herein above. In another embodiment, the invention provides a composition comprising higher molecular weight polycyclic aliphatics (PCA) obtainable by steps a) through d) of a method of the invention. Also provided is a composition comprising a mixture of polycyclic aliphatics (PCA), polyaromatic hydrocarbons (PAH) and/or mono-aromatic polycyclic hydrocarbons (MPH)

15

A composition of the invention typically comprises compounds having a molecular weight in the range of about 100 to 500 Dalton, preferably about 120 to 300 Dalton. In one aspect, the composition comprises compounds having about 9 to 20 C-atoms and single or multiple c rings. Since a method of the invention comprises a (distillation) step to separate a higher molecular weight fraction comprising polyaromatic hydrocarbons (PAH) from a lower molecular weight fraction comprising benzene, toluene and xylene (BTX), a composition provided by the invention typically contains a very small amount, e.g. less than about 10%, preferably less than about 5% by weigh, of monocyclic compounds. This is distinct from compositions known in the art, for example by Zhang *et al.* (2015, Applied Energy, part 150, pp. 128-137). Therein, the production of C8-C15 cyclic alkanes for jet fuels is described via alkylation of low-carbon aromatic monomers obtained from lignocellulose biomass. In contrast to the present invention, the compositions of Zhang mainly consist of (about 80 wt%) alkylated monocyclic structures having an average carbon number of 11.5.

25

30

A composition comprising higher molecular weight PAH, PCA, MPH or mixture thereof finds various uses and applications. For example, a composition comprising higher molecular weight PAH obtainable by steps a) through c) is advantageously used as a biofuel.

- 5 A composition comprising higher molecular weight polycyclic aliphatics (PCA) obtainable by steps a) through d) also has many interesting applications, for example as a jet fuel additive or in a petrochemical process, preferably a process involving a naphtha cracker or a steam reformer. See also Figure 1.

10 The invention is further illustrated by means of the attached drawings and Examples.

LEGEND TO THE FIGURES

15 Fig. 1 is a flow diagram of an embodiment of the method according to the invention for improving the yield of BTX from biomass. The aromatic fraction obtained in the catalytic aromatization treatment is subjected to distillation in order to separate the BTX fraction from a high molecular weight polyaromatic hydrocarbon (PAH) fraction. At least part of the latter fraction is first reduced to a
20 polycyclic aliphatic fraction, which can be co-fed with the biomass in order to achieve a recycling of higher aromatics towards BTX. Alternatively, the high molecular weight fraction (reduced or not) is used for other applications.

Fig. 2 displays the chemistry for the preparation of additional BTX from a polyaromatic fraction by reduction/hydrogenation and subsequent catalytic
25 aromatization.

Fig. 3 and 4 show the ^1H -NMR of the polyaromatic fraction and the ^1H -NMR of the reduced fraction, obtained by catalytic hydrogenation (ex situ upgrading) of glycerol (PAH-1). It clearly displays that the amount of aromatic protons present between 6.5-8.0 ppm are less in intensity and mostly converted to
30 aliphatic (cyclic) hydrocarbons.

Fig. 5 GC Chromatograms of polyaromatic hydrocarbons (from glycerol), polycyclic alkanes/polyaromatic hydrocarbons (PCA/PAH-1), obtained by catalytic

hydrogenation (Ru/C) and PCA/PAH-1 aromatized over an H-ZSM-5 (23) catalyst. It is observed that the PCA/PHA fraction is converted by the catalyst toward a mixture of BTX and higher aromatics.

Fig. 6 and Fig. 7 display the MALDI-TOF spectra of the polyaromatic fraction and the reduced fraction and confirm the transformation of aromatics towards aliphatics.

Fig. 8 is a flow diagram of an embodiment of the method according to the Integrated Cascading Catalytic Pyrolysis (N.J. Schenk, A. Biesbroek, A. Heeres, H.J. Heeres, WO 2015/047085 A1).

Fig. 9 *Ex situ* pyrolysis of polyaromatic hydrocarbons (PAH-2, obtained from glycerol, after distillation of BTX)), polycyclic alkanes/polyaromatic hydrocarbons (PCAG2; , obtained by catalytic hydrogenation (Ru/C) of PAH-2) ((T = 560 C, H-ZSM-5 (23), zeolite : biomass 3 : 1) and an Integrated Cascading Catalytic Pyrolysis Process of PCAG-2 with different cracking catalysts ((T = 560 C, H-ZSM-5 (23), zeolite : biomass 3 : 1, cracking catalyst : biomass = 0.5-1.0 : 1), yields of BTX (see examples 6-19)

It can be concluded that

- the reduced polycyclic and polyaromatic hydrocarbon fraction afford higher yields of BTX as compared to the non-reduced polyaromatic fraction
- both the PAH and PCA fraction suffer from ageing and lowers yields of BTX were obtained if both fractions were stored for several months at room temperature.
- under the conditions used the Integrated Cascading Catalytic Pyrolysis, using a cracking catalyst afforded higher amounts of BTX for fresh produced PCA.
- an *ex situ* pyrolysis of a fresh PCA fraction with a mix of a cracking catalyst and a aromatization catalyst (H-ZSM-5 (23) (layered) results in higher formation of BTX.

Fig 10. Mass balances for the *ex situ* pyrolysis of polyaromatic hydrocarbons (PAH-2, obtained from glycerol, after distillation of BTX)), polycyclic alkanes/polyaromatic hydrocarbons (PCAG2; , obtained by catalytic hydrogenation (Ru/C) of PAH-2) ((T = 560 C, H-ZSM-5 (23), zeolite : biomass 3 : 1) and an Integrated Cascading Catalytic Pyrolysis Process of PCAG-2 with different

cracking catalysts ((T = 560 C, H-ZSM-5 (23), zeolite : biomass 3 : 1, cracking catalyst : biomass = 0.5-1.0 : 1 (see examples 6-19).

It can be concluded that minor amounts of char, gas and water are being formed and the majority of the PAH and PCA is transformed into a bio-oil,
5 consisting of BTX and substituted higher aromatics (GC). The bio-oil obtained can be subjected to distillation in order to isolate BTX and the remaining fraction can be reutilized in the pyrolysis treatment.

Fig 11. displays the BTX yields of the *ex-situ* pyrolysis of several biomass feedstocks co-fed with a polyaromatic hydrocarbon fraction (PAH-2, obtained
10 from glycerol) (see examples 1,6 and 20-22).

Fig 12. shows the yields of BTX for the *ex-situ* pyrolysis of several biomass feedstocks co-fed with a reduced polycyclic and polyaromatic hydrocarbon fraction (PCA, obtained from glycerol). It can be concluded that co-feeding of biomass with an already pyrolyzed fraction results in additional yields of BTX.
15 Furthermore, in most cases a synergistic effect is observed as reflected by a higher yield of BTX from the mixtures than the sum of the yields from the individual feedstocks (see examples 7, 20 and 24-30)

Fig 13. The amount of BTX present in the bio-oil obtained after the *ex-situ* pyrolysis of several biomass feedstocks co-fed with a reduced polycyclic and
20 polyaromatic hydrocarbon fraction (PCA, obtained from glycerol) (see examples 7, 20 and 24-30).

Table 1. Products observed in the GC Chromatograms of polyaromatic hydrocarbons (from glycerol), polycyclic alkanes/polyaromatic hydrocarbons (PCA/PAH-1), obtained by catalytic hydrogenation (Ru/C) and PCA/PAH-1 aromatized over an H-ZSM-5 (23) catalyst

RT	Quality	Glycerol over H-ZSM-5 (23)	PAH	PCA	PCA over H-ZSM-5 (23)
6.06	94	Benzene			Benzene
8.3	90				Cyclohexane, 1,2-dimethyl-, tra
9.87	91	Toluene			Toluene
11.54	94				Cyclohexane, 1,3,5-trimethyl-,
12.86	91				Cyclohexane, 1,2,4-trimethyl-
13.03	96			Cyclohexane, 1,2,4-trimethyl-	Cyclohexane, 1,2,4-trimethyl-
13.17	94				Cyclohexane, 1,2,4-trimethyl-
13.39	95				cis-1-Ethyl-3-methyl-cyclohexan
13.49	90				Cyclohexane, 1-ethyl-4-methyl-,
14.47	93	Ethylbenzene			Ethylbenzene
14.94	97	p-Xylene			Benzene, 1,3-dimethyl-
15.72	91				Cyclohexane, 1-ethyl-2-methyl-,
16.43	97	Benzene, 1,2-dimethyl-			Benzene, 1,2-dimethyl-
17.37	96			1H-Indene, octahydro-, trans-	1H-Indene, octahydro-, trans-
18.42	90				Cyclohexane, 1-methyl-2-propyl-
19.02	95		Decane	Decane	
19.11	91				Cyclohexane, diethyl-

19.3	98				1H-Indene, octahydro-, cis-	1H-Indene, octahydro-, cis-
19.8	91	Benzene, 1-ethyl-2-methyl-				
19.82	90		Benzene, 1-ethyl-3-methyl-		Benzene, 1-ethyl-3-methyl-	
19.87	90		Benzene, 1-ethyl-2-methyl-			
20.2	90	Benzene, 1-ethyl-3-methyl-				
20.21	96				1,2,4-Trimethylbenzene	
20.61	95				Cyclohexane, 1-methyl-2-propyl-	
21	91				Benzene, 1,3,5-trimethyl-	
21.12	90				Cyclohexane, butyl-	
21.72	94	Benzene, 1,2,3-trimethyl-				
21.77	97		1,2,4-Trimethylbenzene		1,2,4-Trimethylbenzene	
21.92	98				1H-Indene, octahydro-5-methyl-	
22.75	99				Naphthalene, decahydro-, trans-	
23.37	98				1H-Indene, octahydro-5-methyl-	
23.54	93		1,2,4-Trimethylbenzene		Benzene, 1,2,3-trimethyl-	
24.22	93		Indane		Indane	
24.26	95			Undecane		
24.86	95				Benzene, 4-ethyl-1,2-dimethyl-	
25.25	99			Naphthalene, decahydro-	Naphthalene, decahydro-	
25.55	95				Naphthalene, decahydro-2-methyl-	
25.67	94		Indene			

25.98	95						Benzene, 4-ethyl-1,2-dimethyl-
26.08	91						Benzene, 1-methyl-4-(1-methylet
26.35	94						Benzene, 2-ethenyl-1,4-dimethyl
26.36	93				Benzene, 1-methyl-2-(2-propenyl)-		
26.43	90				Benzene, 1-ethyl-2,3-dimethyl-		Benzene, 1-ethyl-2,3-dimethyl-
26.44	90					Benzene, 4-ethyl-1,2-dimethyl-	
26.67	90						2,3-Dihydro-1-methylindene
27.65	94						Naphthalene, decahydro-2-methyl
27.92	94						Naphthalene, decahydro-2-methyl
28.15	93				Benzene, 1,2,4,5-tetramethyl-		Benzene, 1,2,4,5-tetramethyl-
28.16	91					Benzene, 4-ethyl-1,2-dimethyl-	
28.4	91				Benzene, 1,2,3,5-tetramethyl-		Benzene, 1,2,4,5-tetramethyl-
29.18	95				Dodecane	Dodecane	
29.38	93						2,3-Dihydro-1-methylindene
29.39	91					Benzene, 2-ethenyl-1,4-dimethyl	
30.14	96						Benzene, 2-ethenyl-1,4-dimethyl
30.15	93					2,3-Dihydro-1-methylindene	
30.73	96				1H-Indene, 1-methyl-		
30.77	96					Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
30.85	96				1H-Indene, 1-methyl-		
31.28	92						Benzene, 2-ethenyl-1,3,5-trimet

31.29	95				1H-Indene, 2,3-dihydro-4,7-dime	
31.41	93			Benzene, (1-methyl-2-cyclopropen-1		
31.47	94			Benzene, (1-methyl-2-cyclopropen-1		
31.54	91				Naphthalene, 1,2,3,4-tetrahydro	
31.54	94					Benzene, (2-methyl-1-butenyl)-
31.8	95				1H-Indene, 2,3-dihydro-1,6-dime	1H-Indene, 2,3-dihydro-4,7-dime
32.01	91					1H-Indene, 2,3-dihydro-1,2-dime
32.24	94					Benzene, (2-methyl-1-butenyl)-
32.25	91				1H-Indene, 2,3-dihydro-1,6-dime	
33.24	96				Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
33.52	94	Naphthalene				
33.55	94		Azulene			Azulene
33.64	94					Naphthalene, 1,2,3,4-tetrahydro
33.79	91					Benzene, 1-(1-methylethenyl)-3-
33.83	95		Tridecane		Tridecane	
34.3	90					1H-Indene, 2,3-dihydro-1,5,7-tr
34.72	96					1H-Indene, 2,3-dihydro-4,7-dime
34.73	90				1H-Indene, 2,3-dihydro-1,3-dime	
35.53	94				Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
36.18	91					Naphthalene, 1,2,3,4-tetrahydro
36.25	90				Benzene, pentamethyl-	Benzene, pentamethyl-

36.54	90					1H-Indene, 2,3-dihydro-4,5,7-tr
36.66	93			1H-Indene, 1,1-dimethyl-		
37.07	92				Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
37.79	93				Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
38.13	90				Naphthalene, 1,2,3,4-tetrahydro	
38.22	95				Tetradecane	
38.57	91		Naphthalene, 1-methyl-			
38.62	94			Naphthalene, 1-methyl-		Naphthalene, 1-methyl-
39.11	94				1,4-Dimethyl-1,2,3,4-tetrahydro	1,4-Dimethyl-1,2,3,4-tetrahydro
39.23	95					1,4-Dimethyl-1,2,3,4-tetrahydro
39.38	94		Naphthalene, 1-methyl	Naphthalene, 1-methyl-		Naphthalene, 1-methyl-
39.56	94				Naphthalene, 6-ethyl-1,2,3,4-te	Naphthalene, 6-ethyl-1,2,3,4-te
39.67	90				Naphthalene, 1,2,3,4-tetrahydro	
40.9	90					3-Ethyl-3-phenyl-1-pentene
41.09	90			Benzene, 1,3,5-trimethyl-2-(1,2-pr		
41.24	96				Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
42.36	96			Pentadecane	Pentadecane	
42.76	97			Naphthalene, 1-ethyl-		
43.21	95				Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
43.26	94		Naphthalene, 1,7-dimethyl-			
43.3	98			Naphthalene, 2,6-dimethyl-		

43.3	96					Naphthalene, 1,7-dimethyl-
43.31	91				Naphthalene, 1,2,3,4-tetrahydro	
43.91	93	Naphthalene, 1,7-dimethyl-				
43.95	98		Naphthalene, 1,8-dimethyl-			
43.95	98					Naphthalene, 2,6-dimethyl-
44.04	91	Naphthalene, 2,6-dimethyl-				
44.08	97		Naphthalene, 2,6-dimethyl-			Naphthalene, 2,6-dimethyl-
44.98	96		Naphthalene, 1,3-dimethyl-			Naphthalene, 1,3-dimethyl-
45.58	90		Naphthalene, 1,2-dimethyl-			
47.17	91		Naphthalene, 1,4,6-trimethyl-			Naphthalene, 1,4,6-trimethyl-
48.14	93		Naphthalene, 1,6,7-trimethyl-			Naphthalene, 1,6,7-trimethyl-
48.3	95		Naphthalene, 1,6,7-trimethyl-			Naphthalene, 1,6,7-trimethyl-
48.95	96					Naphthalene, 1,4,5-trimethyl-
48.97	93		Naphthalene, 1,6,7-trimethyl-			
49.28	96		Naphthalene, 1,6,7-trimethyl-			
49.28	97					Naphthalene, 1,4,6-trimethyl-
49.72	93					Naphthalene, 1,4,6-trimethyl-
49.88	96		Naphthalene, 1,6,7-trimethyl-			
49.88	95					Naphthalene, 2,3,6-trimethyl-
50.41	95					Naphthalene, 1,4,6-trimethyl-
53.73	91					Azulene, 7-ethyl-1,4-dimethyl-

54.24	94					Azulene, 7-ethyl-1,4-dimethyl-
54.43	98				Phenanthrene, 1,2,3,4,5,6,7,8-o	
55.15	91					4,4'-Dimethylbiphenyl
55.4	93					4,4'-Dimethylbiphenyl
55.48	91					4,4'-Dimethylbiphenyl
56.54	91					Tricyclo[4.4.1.0 ^{2,5}]undeca-1(10
67.31	91					Phenanthrene, 2,5-dimethyl-

The invention is further illustrated by means of the following non-limiting examples.

EXPERIMENTAL SECTION

5

Example 1: *Catalytic aromatization of glycerol (ex situ upgrading, gram scale)*

Crude glycerol was obtained from a biodiesel production process. The crude glycerol was first pyrolysed and subsequently *in situ* up-graded using a bench-scale reactor set up comprising a pyrolysis- and an up-grading unit, connected with each other. A constant stream of N₂ of about 11 min/ml was used as a gas flow in order to maintain an inert atmosphere. The pyrolysis unit was filled with crude glycerol (0.94 g) and the upgrading unit was filled with the catalyst (H-ZSM-5 (23), 3.18 g). The up-grading unit of the bench-scale reactor set up, including the catalyst, was first placed in a fluidized sand bed (T = 550°C) and after reaching T = 550 ° C the pyrolysis unit, comprising the crude glycerol, was placed in the fluidizing bed to start the vaporization/pyrolysis. The pyrolysis took about 5-15 min to finish (constant N₂ flow). The obtained glycerol liquor gas is subsequently converted in the upgrading unit via the catalytic treatment. The converted glycerol liquor gas was subsequently condensed by cooling the vapour phase to a temperature of -40°C. The amount of condensables was determined by weight. The cooling unit was then washed with small amounts of THF, the amount of water was determined using Karl Fischer titration and the organic fraction was subsequently calculated by difference.

25

Example 2 : *Catalytic aromatization of glycerol (ex situ upgrading, > 100 gram scale)*

Crude glycerol was evaporated/pyrolyzed/aromatized in a demo reactor comprising a evaporation/pyrolysis unit (reactor 1, T = 520 °C), a fixed bed containing the aromatization catalyst (reactor 2, H-ZSM-5 (23)/bentonite 60 : 40, 200 gram, 1-2 mm particles, T = 536 °C,) and a condenser zone (T = -20 °C). The glycerol was heated to T = 70° C and fed (850 gram, 3.8 g/min) to the first reactor using a N₂ flow (1.5 L/min). Layer separation of the condensed fraction

30

(organics/water) afforded an aromatic oil (163.2 g; about 70 g BTX, based on GC)) and water (215,45 g).

Example 3: *Distillation of the aromatic oil*

5 Combined crude aromatic bio-oils (3.5 liter) from example 2 were transferred to a separating funnel and the phases were allowed to settle over the weekend. The phases were separated and the crude bio-oil was dried over Na₂SO₄ and subsequently filtered by suction over a glass-filter. The filtered oil (2941 g) was subjected to a coarse distillation under reduced pressure (1000 mbar @ 50 mbar
10 and 40 °C @ 110 °C using a simple distilling setup and a 3-4 L distilling flask, affording a mixture of benzene, toluene and xylenes (1193 g) and a residual oil (1748 g) consisting of higher molecular weight aromatics (polyaromatic hydrocarbons)

15 **Example 4: *Catalytic hydrogenation of substituted polyaromatic hydrocarbons (PAH-1)***

A polyaromatic hydrocarbon fraction, obtained according to Example 3 (PAHG1; 15.02 g), and 5% Ru/C (0.76 g; Sigma-Aldrich) were put under hydrogen pressure (101.5 bar) in a Parr apparatus and heated to 305°C (external
20 temperature, P=119.1 bar). A gradual pressure drop in H₂ pressure was observed. After stirring for 2 hrs the reaction was cooled to room temperature and the reaction product was filtered over cotton wool (3x) and Na₂SO₄ (1x), affording an orange oil (5 g).

25 **Example 5 : *Catalytic hydrogenation of substituted polyaromatic hydrocarbons (PAH-2)***

A polyaromatic hydrocarbon fraction, obtained according to Example 3 (PAHG2; 18.01 g), and 5% Ru/C (0.92 g) were put under hydrogen pressure (134.1 bar) in a Parr apparatus and heated to 305°C (external temperature, P=119.1 bar).
30 A gradual pressure drop in H₂ pressure was observed. After stirring for 3,25 hrs the reaction was cooled to room temperature and the reaction product was filtered over Whatman syringe filters (0.2µm) affording an orange oil (11.6 g).

Example 6: Catalytic aromatization of substituted polyaromatic hydrocarbons (ex situ upgrading, PAH2, gram scale)

Under identical conditions as described in Example 1 a substituted polyaromatic fraction (prepared according to Example 3, 1.05 gram) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.04 g).

Example 7: Catalytic aromatization of substituted polycyclic aliphatic hydrocarbons/polyaromatic hydrocarbons (ex situ upgrading, PCA-2, gram scale)

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (PCAG2, prepared according to Example 5, 0.87 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.01 g).

Example 8: Integrated cascading catalytic pyrolysis of a reduced polyaromatic hydrocarbon fraction (PCAG2) with bentonite (ex situ upgrading, gram scale)

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.52 g) mixed with bentonite (0.54 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (1.55 g).

Example 9: Integrated cascading catalytic pyrolysis of a reduced polyaromatic hydrocarbon fraction (PCAG2) with hydrotalcite (ex situ upgrading, gram scale)

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.57 g) mixed with hydrotalcite (0.48 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (2.09 g).

Example 10: Integrated cascading catalytic pyrolysis of a reduced polyaromatic hydrocarbon fraction (PCAG2) with phosphotungstic acid hydrate (ex situ upgrading, gram scale)

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.52 g) mixed

with phosphotungstic acid hydrate (0.25 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (1.59 g).

**Example 11: Integrated cascading catalytic pyrolysis of a reduced
5 polyaromatic hydrocarbon fraction (PCAG2) with MnO₂ (ex situ
upgrading, gram scale)**

Under identical conditions as described in Example 1 a reduced
polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.51 g) mixed
with MnO₂ (0.27 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (1.64 g).

10

**Example 12: Integrated cascading catalytic pyrolysis of a reduced
polyaromatic hydrocarbon fraction (PCAG2) with FeO (ex situ upgrading,
gram scale)**

Under identical conditions as described in Example 1 a reduced
15 polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.48 g) mixed
with FeO (0.28 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (1.87 g).

**Example 13: Integrated cascading catalytic pyrolysis of a reduced
polyaromatic hydrocarbon fraction (PCAG2) with silicotungstic acid (ex
20 situ upgrading, gram scale)**

Under identical conditions as described in Example 1 a reduced
polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.47 g) mixed
with silicotungstic acid (0.33 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst
(1.71 g).

25

**Example 14: Integrated cascading catalytic pyrolysis of a reduced
polyaromatic hydrocarbon fraction (PCAG2) with ASA1/Siral 40 (ex situ
upgrading, gram scale)**

Under identical conditions as described in Example 1 a reduced
30 polyaromatic hydrocarbon fraction (PCAG2, according to Example 5, 0.45 g) mixed
with ASA1/Siral 40 (0.49 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst
(1.74 g).

Example 15: Catalytic aromatization of substituted polycyclic aliphatic hydrocarbons/polyaromatic hydrocarbons (ex situ upgrading, PCA-2, gram scale, fresh material)

Under identical conditions as described in Example 1 a reduced
5 polyaromatic hydrocarbon fraction (PCAG2, fresh material, prepared according to Example 5, 0.99 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.05 g).

Example 16: Integrated cascading catalytic pyrolysis of a reduced polyaromatic hydrocarbon fraction (PCAG2, fresh material)) with FeO (ex situ upgrading, gram scale)
10

Under identical conditions as described in Example 1 a polyaromatic hydrocarbon fraction (according to Example 5, Inouk 0.87 g) mixed with FeO (0.35 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.03g).

Example 17: Ex situ pyrolysis of a reduced polyaromatic hydrocarbon fraction with FeO₂/H-ZSM-5 (23), layered.
15

Under identical conditions as described in Example 1 a polyaromatic hydrocarbon fraction (according to Example 5, 0.86 g) was pyrolyzed and catalytically aromatized with a catalyst consisting of FeO (first layer, 0.71 g) and
20 H-ZSM-5 (23) (second layer, 3.15 g)

Example 18: Integrated cascading catalytic pyrolysis of a reduced polyaromatic hydrocarbon fraction (PCAG2, fresh material) with ASA1/Siral 40 (ex situ upgrading, gram scale)
25

Under identical conditions as described in Example 1 a polyaromatic hydrocarbon fraction (according to Example 5, 1.10 g) mixed with ASA1/Siral 40 (Inouk 0.77g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.63 g).

Example 19: Ex situ pyrolysis of a reduced polyaromatic hydrocarbon fraction (PCAG2, fresh material) with ASA1/Siral 40 /H-ZSM-5 (23), layered.
30

Under identical conditions as described in Example 1 a polyaromatic hydrocarbon fraction (according to Example 5, 1.02 g) was pyrolyzed and

catalytically aromatized with a catalyst consisting of ASA1/Siral 40 (first layer, 0.70 g) and H-ZSM-5 (23) (second layer, 3.40 g)

5 **Example 20: Catalytic aromatization of wood (ex situ upgrading, gram scale)**

Under identical conditions as described in Example 1 pinewood (0.85 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (2.63 g).

10 **Example 21: Catalytic aromatization of a mixture of pinewood and substituted polyaromatic hydrocarbons (hydrocarbons (PAH-2), ratio 1:1 (ex situ upgrading, gram scale)**

Under identical conditions as described in Example 1 a polyaromatic hydrocarbon fraction (PAH-2, according to Example 3, 0.62 g) mixed with pinewood (0.56 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.64 g).

15

Example 22: Catalytic aromatization of a mixture of glycerol and substituted polyaromatic hydrocarbons (hydrocarbons (PAH-2), ratio 1:1 (ex situ upgrading, gram scale)

20 Under identical conditions as described in Example 1 a polyaromatic hydrocarbon fraction (according to Example 3, 0.57 g) mixed with glycerol (0.40 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.29 g).

25 **Example 23: Catalytic aromatization of a mixture of glycerol and a reduced polyaromatic hydrocarbon fraction (hydrocarbons (PCAG-2), ratio 1:1 (ex situ upgrading, gram scale)**

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (according to Example 5, 0.43 g) mixed with glycerol (0.40 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.17 g).

30 **Example 24: Catalytic aromatization of a mixture of wood and a reduced polyaromatic hydrocarbon fraction (PCAG2), ratio 1:1 (ex situ upgrading, gram scale)**

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (prepared according to Example 5, 0.61 g) mixed with wood (0.50 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.33 g).

5 **Example 25: Catalytic aromatization of Kraft lignin (*ex situ* upgrading, gram scale)**

Under identical conditions as described in Example 1 Kraft lignin (1.00 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.37 g).

10 **Example 26: Catalytic aromatization of a mixture of Kraft lignin and a reduced polyaromatic hydrocarbon fraction (PCAG2), ratio 1:1 (*ex situ* upgrading, gram scale)**

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (prepared according to Example 5, 0.55 g) mixed with Kraft lignin (0.51 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.29 g).

Example 27: Catalytic aromatization of cellulose (*ex situ* upgrading, gram scale)

Under identical conditions as described in Example 1 cellulose (1.00 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (2.96 g).

Example 28: Catalytic aromatization of a mixture of cellulose and a reduced polyaromatic hydrocarbon fraction (PCAG2), ratio 1:1 (*ex situ* upgrading, gram scale)

Under identical conditions as described in Example 1 a reduced polyaromatic hydrocarbon fraction (prepared according to Example 5, 0.53 g) mixed with cellulose (0.53 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.79 g).

30 **Example 29: Catalytic aromatization of Jatropha oil (*in situ* upgrading, gram scale)**

Under identical conditions as described in Example 1 Jatropha oil (1.28 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.87 g).

Example 30: *Catalytic aromatization of a mixture of Jatropha oil and a reduced polyaromatic hydrocarbon fraction (PCAG2), ratio 1:1 (ex situ upgrading, gram scale)*

- Under identical conditions as described in Example 1 a reduced
- 5 polyaromatic hydrocarbon fraction (prepared according to Example 5, 0.51 g) mixed with Jatropha oil (0.52 g) was *ex-situ* pyrolyzed with a H-ZSM-5 (23) catalyst (3.79 g).

CLAIMS

1. A process for the preparation of aromatic compounds from a feed stream containing biomass or mixtures of biomass, the process comprising:
 - 5 a) subjecting a feed stream containing biomass or mixtures of biomass to a process to afford a conversion product comprising aromatic compounds;
 - b) recovering the aromatic compounds from said conversion product;
 - c) separating a higher molecular weight fraction comprising polyaromatic hydrocarbons (PAH) from a lower molecular weight fraction comprising benzene,
10 toluene and xylene (BTX) by distillation;
 - d) reducing at least part of said higher molecular weight fraction to obtain a reduced fraction comprising polycyclic aliphatics (PCA); and
 - e) subjecting the higher molecular weight fraction obtained in step c), the reduced fraction obtained in step d), or a mixture thereof, to a process to obtain
15 lower molecular weight aromatics (BTX).
2. Process according to claim 1, wherein step a) comprises subjecting the biomass feed stream to *in situ* or *ex situ* pyrolysis, or to a vaporization process.
3. Process according to claim 2, wherein step a) comprises pyrolysis of the biomass feed, preferably using a cheap cracking catalyst, followed by subsequently
20 subjecting the vapors thus obtained to an *ex situ* catalytic aromatization step.
4. Process according to any one of claims 1-3, wherein said feed stream containing biomass or mixtures of biomass comprises one or more of selected from the group consisting of agricultural waste, plants, wood, preferably wherein the feed stream comprises organic material such as, glucose, maltose, starch,
25 cellobiose, cellulose, hemi-cellulose, other polysaccharides, lignin, sugar cane bagasse, lignocellulosic materials (e.g., wood chips or shavings, lignocellulosic biomass, etc.), glycerol, fatty acids, fatty acid methyl esters, triglycerides, food waste, animal waste, manure, corn stover, partially decayed vegetation, such as peat or lignite, or any combination thereof.

5. Process according to any one of claims 1-4, wherein step a) comprises adding at least one further reactant to the feed stream, the reactant being selected from the group consisting of olefins, alcohols, aldehydes, ketones, acids and combinations thereof.
- 5 6. Process according to claim 5, wherein the further reactant comprises 1 to 6 carbon atoms, preferably wherein the further reactant is selected from the group consisting of ethene, propene, butene, isobutene, pentenes, hexenes, methanol, ethanol, propanol, isopropanol, hexanol, formaldehyde, acetaldehyde, acetone, methyl ethyl ketone, formic acid and acetic acid.
- 10 7. Process according to any one of claims 1-6, wherein step d) comprises catalytic hydrogenation, preferably using a catalyst selected from the group consisting of Ru/C, Ni/C, Pd/C, Pt/C, MoS₂, WS₂, Co-Mo-S/Al₂O₃, Ni-Mo-S/Al₂O₃, Ni-W-S/Al₂O₃, Co-Mo/Al₂O₃ or homogeneous catalysts such as the Wilkinson catalyst and the Crabtree catalyst.
- 15 8. Process according to claim 7, wherein said catalytic hydrogenation is performed without the addition of a solvent.
9. Process according to any one of 1-8, wherein step e) comprises mixing the higher molecular weight fraction obtained in step c) or the reduced fraction obtained in step d) with a biomass feedstream and subjecting the resulting mixture
20 to pyrolysis or vaporization.
10. Process according to claim 9, wherein the process of step e) comprises a catalytic pyrolysis treatment.
11. Process according to claim 9 or 10, comprising mixing the higher molecular weight fraction obtained in step c) or the reduced fraction obtained in
25 step d) with the biomass feedstream of step a).
12. A composition comprising higher molecular weight polyaromatic hydrocarbons (PAH) obtainable by steps a) through c) of a method of any one of claims 1-6.

13. A composition comprising higher molecular weight polycyclic aliphatics (PCA) obtainable by steps a) through d) of a method of any one of claims 1-8.
14. Composition according to claim 12 or 13, comprising up to 10 wt% of monocyclic compounds.
- 5 15. Composition according to claim 13 or 14, wherein said composition comprises a mixture of polycyclic aliphatics (PCA) and polyaromatic hydrocarbons (PAH).
16. Composition according to any one of claims 12 to 15, wherein said composition comprises compounds having a molecular weight in the range of about
10 100 to 500 Dalton, preferably about 120 to 300 Dalton.
17. Composition according to any one of claims 12-16, wherein said composition comprises compounds having about 9 to 20 C-atoms and multiple aromatic rings.
18. Use of a composition according to any one of claims 12-17 as a biofuel.
- 15 19. Use of a composition according to claim 13-17 as a jet fuel additive.
20. Use of a composition according to claim 13-17 in a petrochemical process, preferably a process involving a naphtha cracker or a steam reformer.

Figure 1

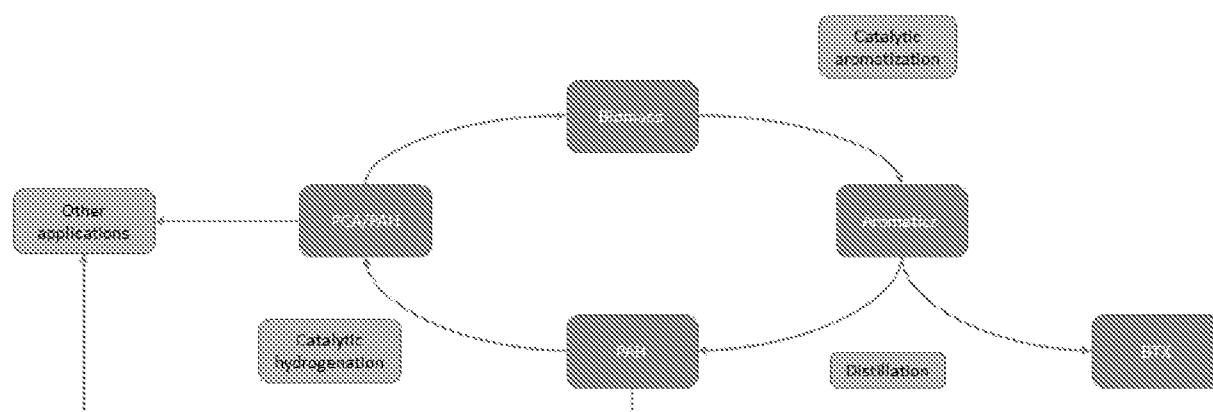


Figure 2

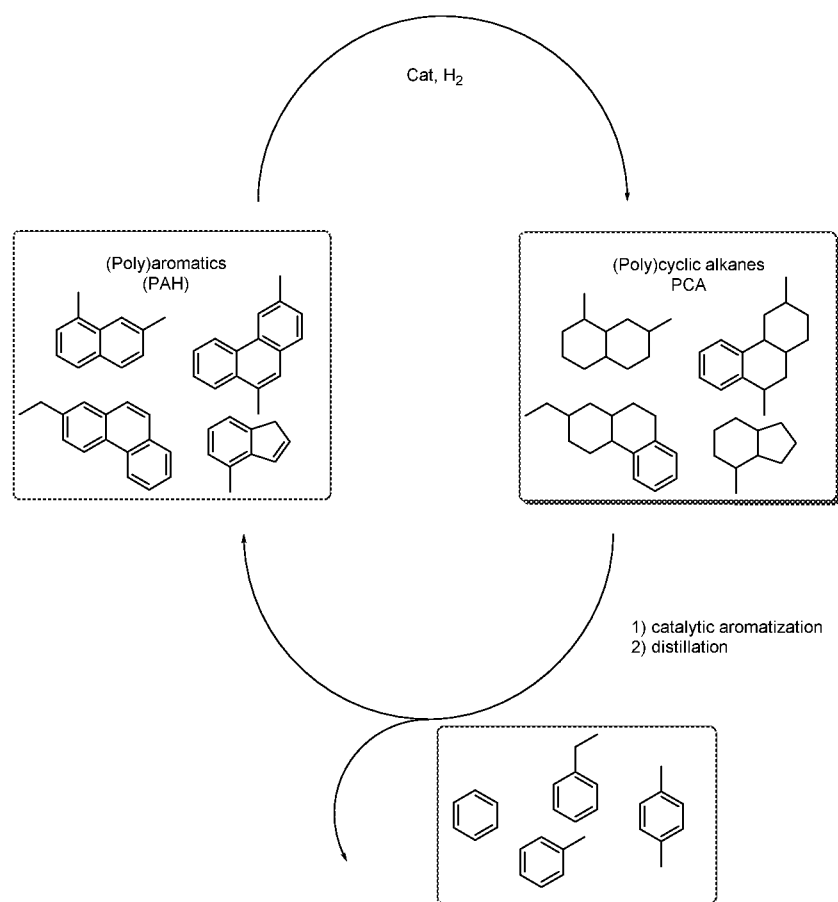


Figure 3

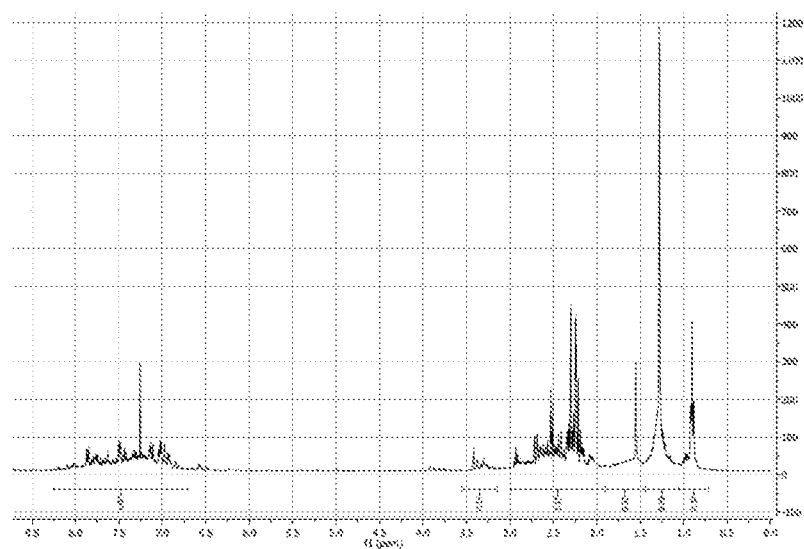


Figure 4

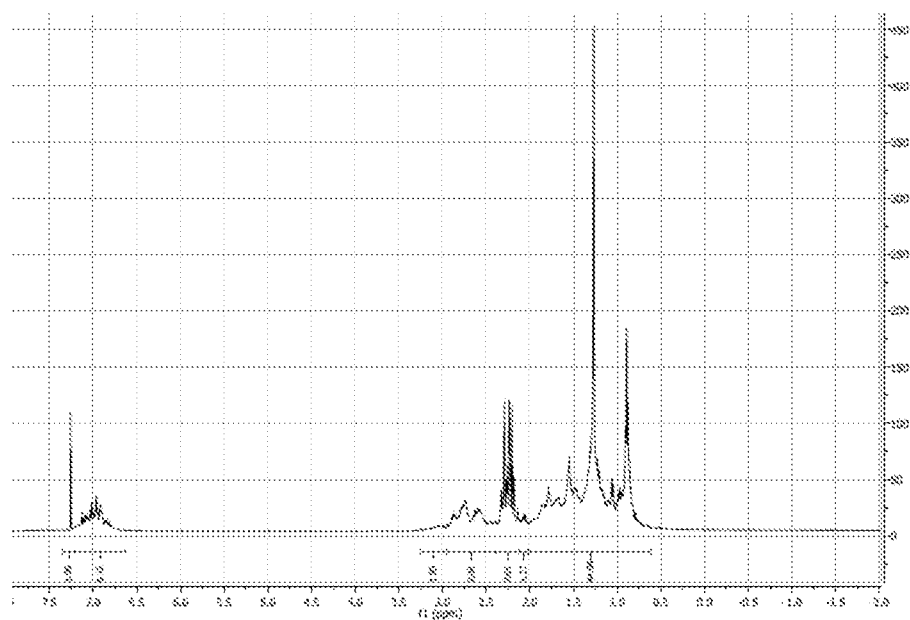


Figure 5

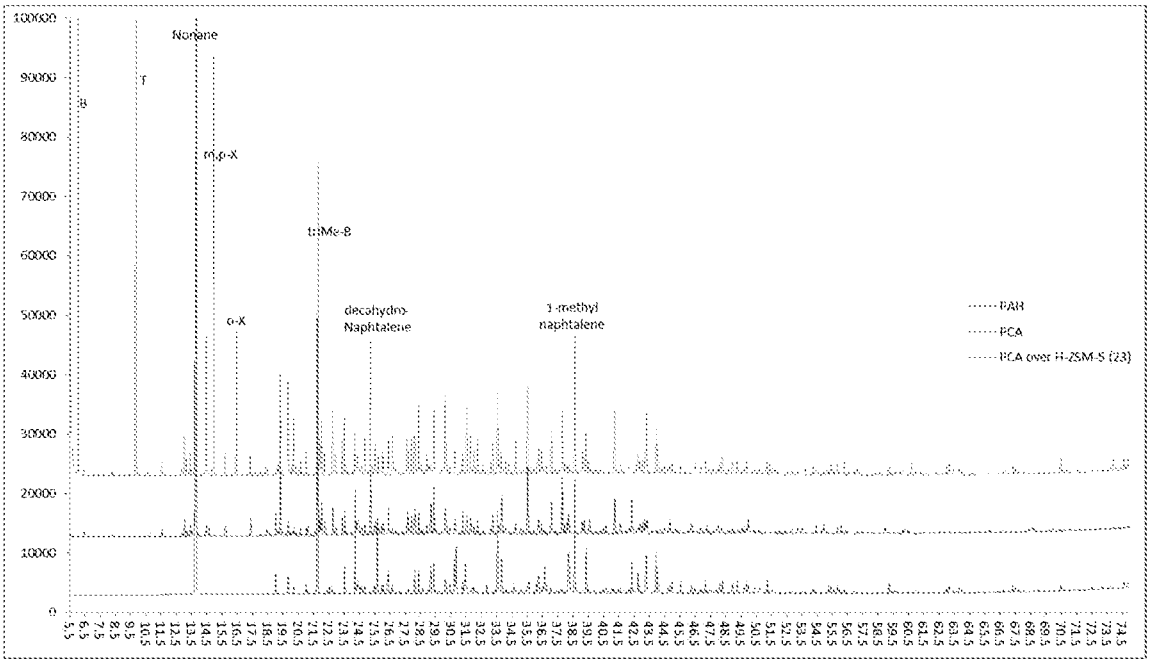


Figure 6

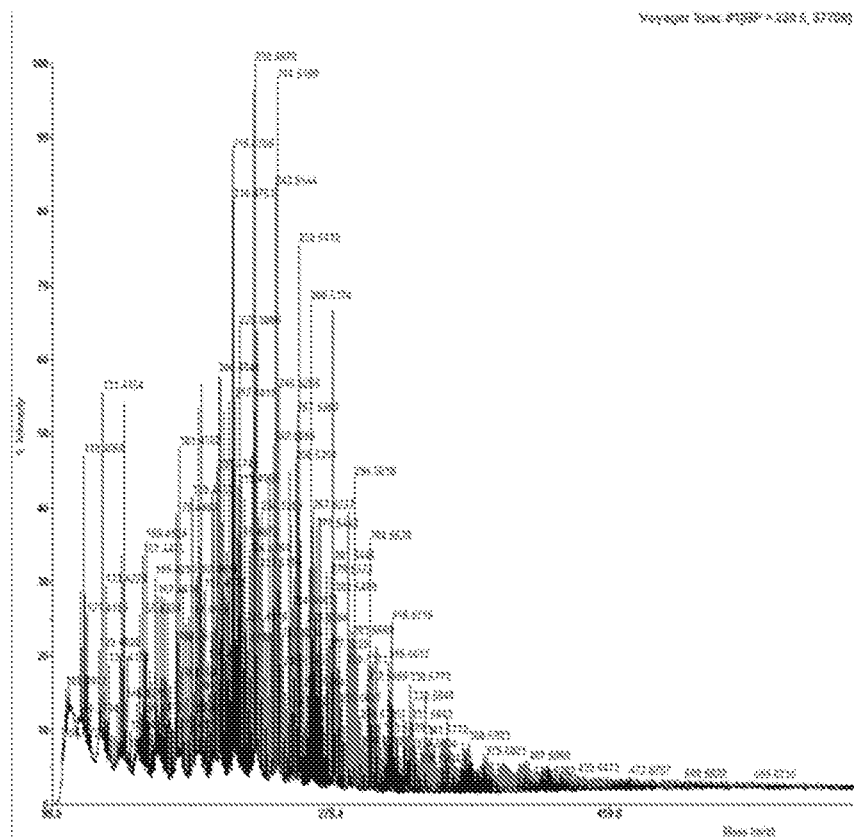


Figure 7

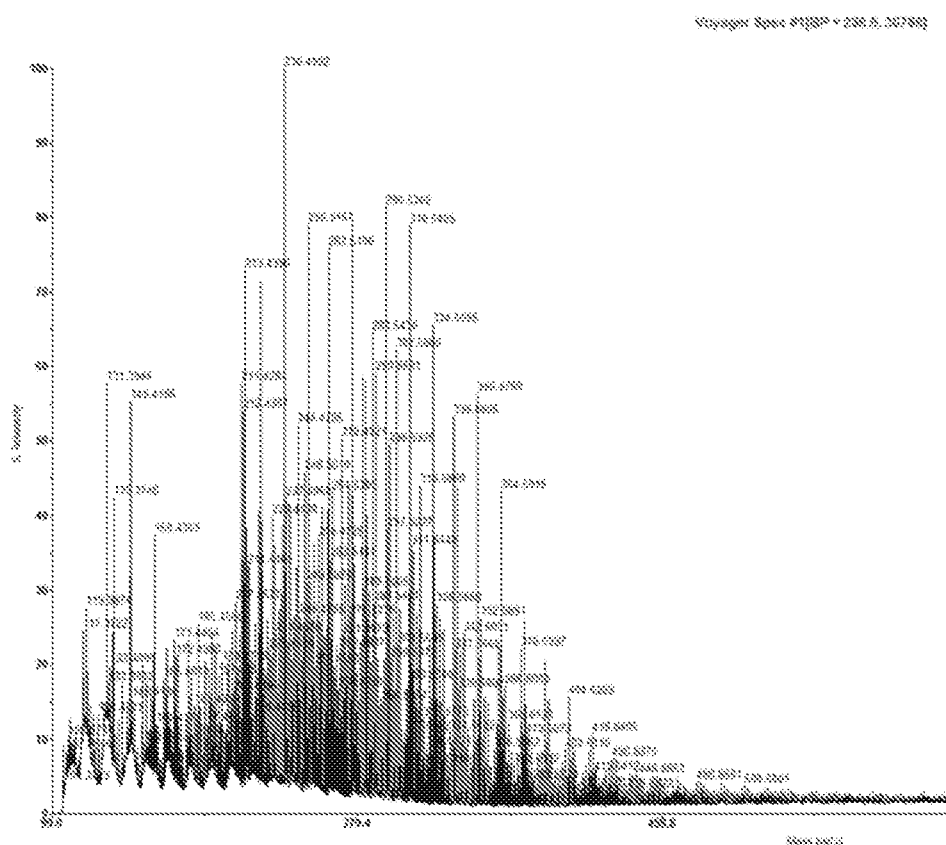


Figure 8

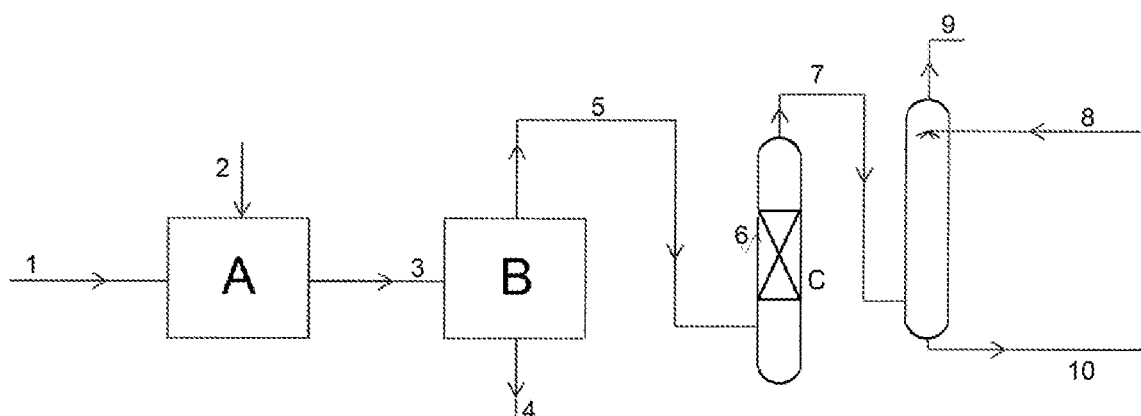


Figure 9.

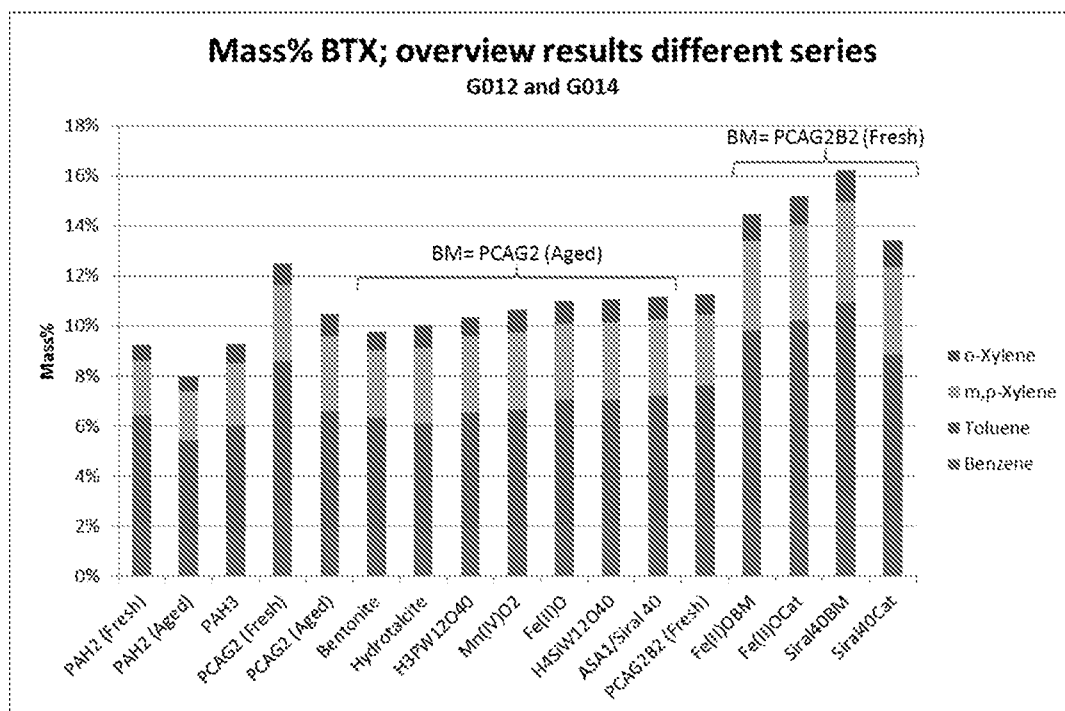


Figure 10

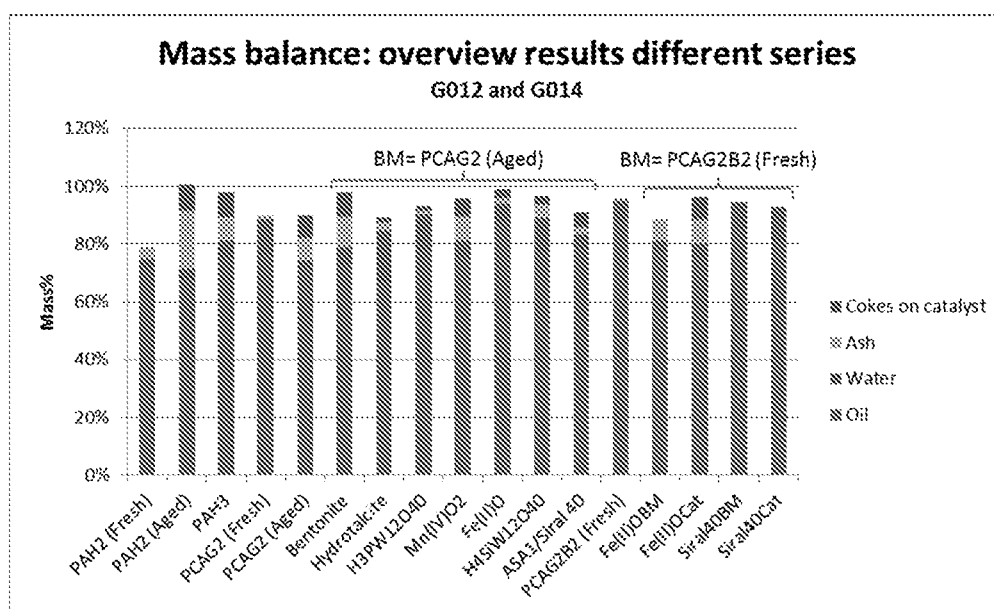


Figure 11

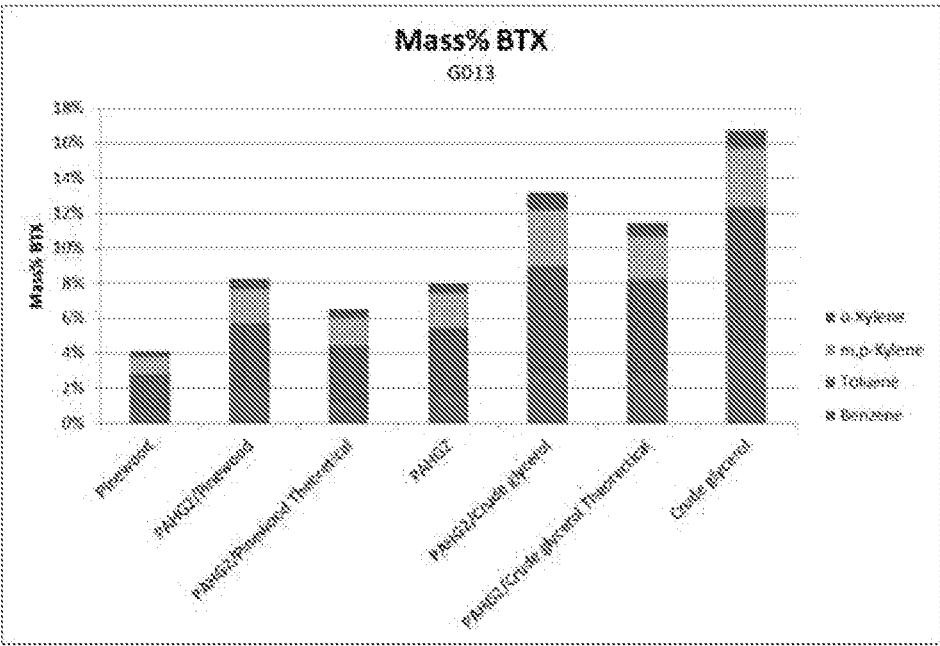


Figure 12

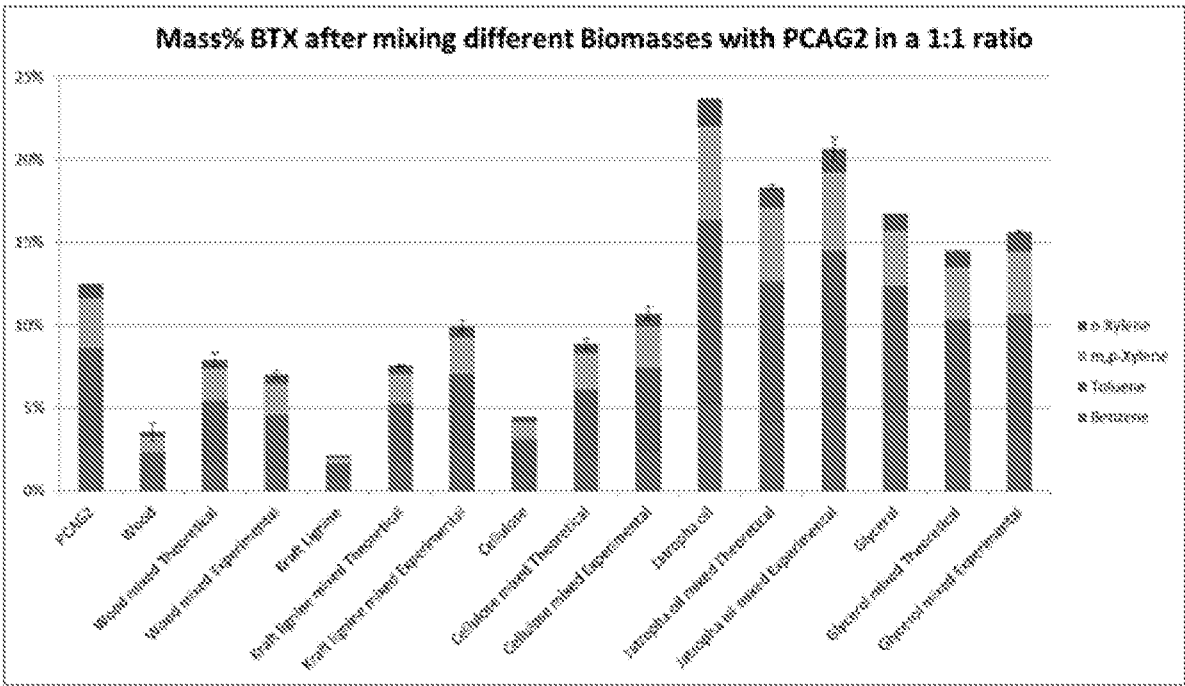
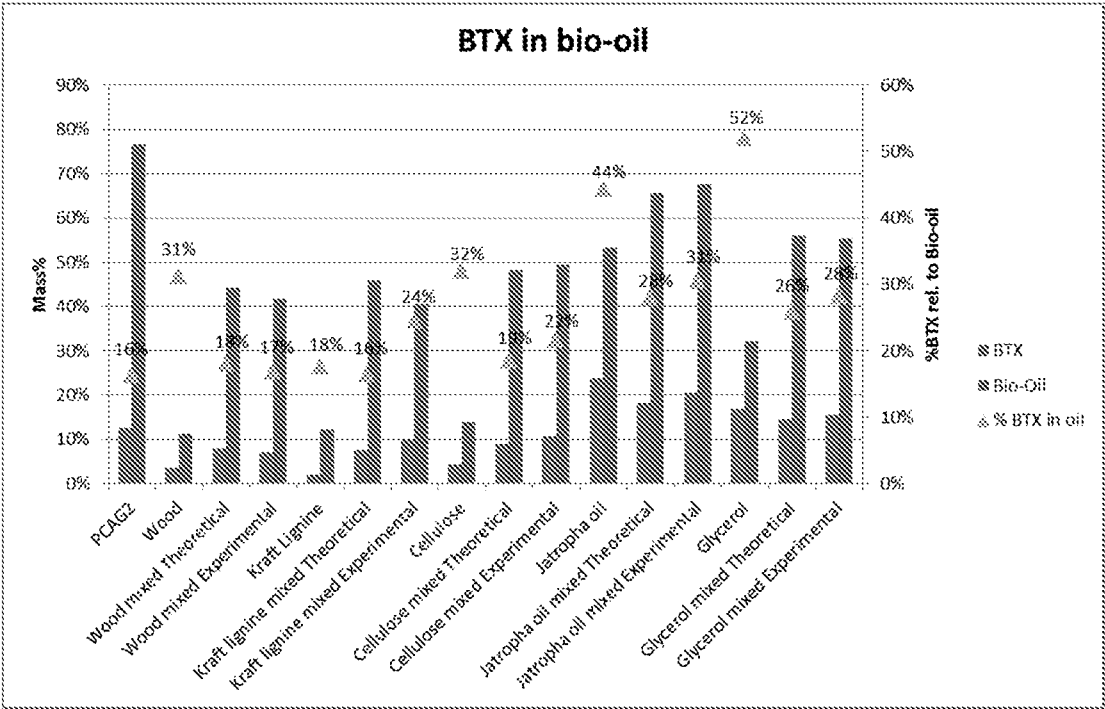


Figure 13



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2017/050419

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C10G1/00	C10G1/02 C10G1/08 C10B53/02 C10G45/44
	C10G45/46	
ADD.		
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)		
C10G C10B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/002162 A1 (TANZIO MICHAEL [US] ET AL) 7 January 2016 (2016-01-07) paragraphs [0041], [0042], [0045], [0048]; figures 1,3	1-17
A	US 2013/172639 A1 (YANAGAWA SHINICHIRO [JP] ET AL) 4 July 2013 (2013-07-04) paragraphs [0004] - [0008], [0167]	1-20
	-/--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* 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		Date of mailing of the international search report
28 July 2017		07/08/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Gzil, Piotr

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2017/050419

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHANG YAJING ET AL: "Production of jet and diesel biofuels from renewable lignocellulosic biomass", APPLIED ENERGY, vol. 150, 20 April 2015 (2015-04-20), pages 128-137, XP029235915, ISSN: 0306-2619, DOI: 10.1016/J.APENERGY.2015.04.023 cited in the application page 132	12-20
A	----- André Heeres ET AL: "BioBTX aims for production of aromatics by catalytic pyrolysis of biomass and plastic waste", PyNe Issue 34, 1 January 2014 (2014-01-01), pages 13-14, XP055159953, Retrieved from the Internet: URL: http://www.pyne.co.uk/Resources/user/PyNe Newsletter Issue 34 January 14 PUBLISHED.pdf [retrieved on 2015-01-05] the whole document	1-20
A	----- WO 2015/047085 A1 (BIOBTX B V [NL]; UNIV GRONINGEN [NL]; KNN ADVIES B V [NL]; SYNCOM B V) 2 April 2015 (2015-04-02) cited in the application the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2017/050419

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016002162	A1	07-01-2016	
		AU 2015284065 A1	02-02-2017
		CA 2953141 A1	07-01-2016
		CN 106574190 A	19-04-2017
		EP 3164465 A2	10-05-2017
		KR 20170052561 A	12-05-2017
		US 2016002162 A1	07-01-2016
		WO 2016004248 A2	07-01-2016

US 2013172639	A1	04-07-2013	
		CN 103097496 A	08-05-2013
		EP 2617797 A1	24-07-2013
		JP 5535845 B2	02-07-2014
		JP 2012062356 A	29-03-2012
		KR 20130106826 A	30-09-2013
		SG 188970 A1	31-05-2013
		US 2013172639 A1	04-07-2013
		WO 2012036186 A1	22-03-2012

WO 2015047085	A1	02-04-2015	NONE
