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Alternative Method for the Production of Second-Generation Biofuels

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5 Direct coal liquefaction (DCL) is an industrial technology for the production of liquid fuels by high-pressure and high-temperature hydroconversion of coal. The technique can also be applied to biocoals produced by hydrothermal carbonization (HTC) of biomass waste. The biofuels produced
10 are promising with regard to H/C molar ratio, higher heating value and oxygen content.

The rapid depletion of the reserves and resources of crude oil and the increasing price per barrel enforces the consideration of alternatives for the fuel sector. Intensively discussed is the
15 production of second-generation biofuels which are not so much interfering with food supplies and biodiversity. The conventional routes followed are either the gasification of biomass to synthesis gas followed by Fischer-Tropsch synthesis, or the pyrolysis or liquefaction of biomass to biooil, an unstable oil, which usually
20 has to be stabilized fast by hydrodeoxygenation or zeolite upgrading (see Fig. 1) ¹. A combination of these conventional routes is the bioliq[®] process where the biomass is subjected to fast pyrolysis. The thus produced biooil is afterwards gasified and then further converted to fuels via methanol/dimethyl ether ². We
25 present an alternative route as shown in Figure 1, which goes back to the work of Friedrich Bergius. He realized that direct coal liquefaction at high temperatures and hydrogen pressures is not only possible with coal but also with biomass, especially with biocoal obtained by hydrothermal carbonization, a process which
30 simulates the coalification process ³. However, direct biocoal liquefaction has never been considered for commercial application. Only biochar, a by-product of biomass pyrolysis, has been tested as feedstock for direct liquefaction ⁴. Since hydrothermal carbonization (HTC) has nowadays obtained
35 renewed interest and can be well controlled ⁵⁻⁷, also the direct liquefaction of HTC coal should be evaluated. So far, the biocoal obtained by HTC is only considered for combustion, gasification, carbon fixation, soil amendment or production of carbon materials ⁵⁻⁷.

40 Biomass as a feedstock has several economic drawbacks: Logistically, the high moisture content of 14 wt.-% (rice straw) up to 45 wt.-% (wood chips) reduces the number of dry metric tons per load and therefore increases the transportation costs since they are charged per actual metric ton ⁸⁻⁹. Furthermore,
45 storage of biomass is not trivial since storage of wet biomass can cause significant loss of biomass, quality degradation and even danger ¹⁰. The process efficiency of biomass gasification at temperatures > 873 K suffers from the additional energy needed to evaporate the high moisture content for reaching optimal
50 process conditions. Albeit waste heat can be used for drying, water evaporation is very energy-intensive ¹¹. Biomass pyrolysis occurs at atmospheric pressure and temperatures between 573 and

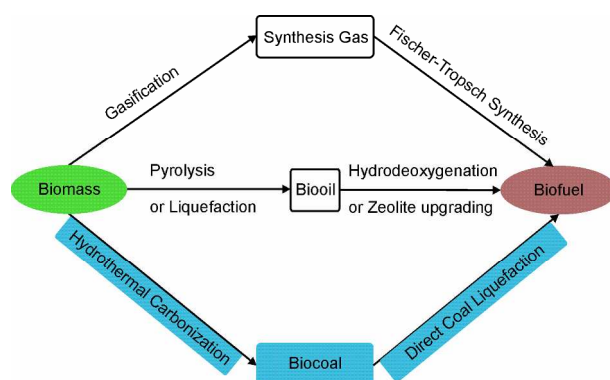


Fig. 1 Different routes for the production of second-generation biofuels from biomass; in white: conventional routes, in blue: alternative route.

55 3273 K yielding pyrolysis oil, and usually the biomass has to be dried and ground before pyrolysis, which is also very energy-intensive ¹.

Our proposal of an alternative method for the production of biofuels comprises the conversion of biomass in small
60 decentralized plants into a biocoal by HTC which has a better efficiency of transportation to a central direct coal liquefaction (DCL) plant where valuable biofuels can be produced. HTC is a process where wet biomass is transformed into a lignite-like biocoal at temperatures between 453 and 568 K ^{5-7,12,13}. The
65 biomass feedstocks for HTC are manifold and can be crop wastes, effluent sludge, manure, food waste, municipal solid waste, grass, leaves, straw, bark and wood ^{5-7,12,13}. In the CarboREN process, biomass (green wastes) can be converted into biocoal with an efficiency of 95 % ⁵. The product, namely
70 Biocoal A, is one of the two coals we used in our experiments for direct biocoal liquefaction. The second biocoal, "Biocoal B", was provided by SmartCarbon AG and was made out of horse manure via HTC. Table 1 shows the proximate and ultimate analysis data whereby the moisture in the biocoals is only 2 to 4 wt.-% which
75 results in a much better transport efficiency (dry metric tons per load) than for raw biomass (untreated wood, 19.8 wt.-%) and lignite (36.5 wt.-%) ^{11,14}. Differences in ultimate and proximate analysis between the biocoals are owed to different ways of HTC processing. Table 1 further shows that the carbon contents of the
80 moisture- and ash-free (maf) biocoals (54.6 to 70.9 wt.-%) are higher than those of lignite (52.4 wt.-%) and untreated wood (50.8 wt.-%). The comparatively higher mass of organic carbon per maf weight in biocoals is reflected by an increase in higher heating values (22.6 to 31.8 MJ kg⁻¹ as compared to 20.6 and 21.3
85 MJ kg⁻¹ for untreated wood and lignite, respectively). Correspondingly, such values indicate the possibility of having higher hydrocarbon yields with

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Table 1 Proximate and ultimate analysis of untreated wood and lignite and different biocoals produced by HTC (Biocoals A and B (this work), Biocoals C to G from literature) with the corresponding higher heating values (*HHV*).

Material	Ultimate Analysis ^a / wt.-%					<i>HHV</i> ^b / MJ kg ⁻¹	HTC conditions	Proximate Analysis ^c / wt.-%	
	C	H	N	S	O ^d			Moisture	Ash
Untreated Wood ¹¹	50.8	6.1	0.4	0.1	42.6	20.6	-	19.8	1.8
Lignite ¹⁴	52.4	5.5	2.2	2.7	37.2	21.3	-	36.5	38.4
Biocoal A (from green waste, this work)	57.4	5.5	0.2	0 ^e	36.9	22.6	473 K, several hours	3.2	1.4
Biocoal B (from horse manure, this work)	68.8	5.9	2.6	0.2	22.5	28.6	483 K, 4-8 h	2.3 ^f	19.8
Biocoal C (from straw) ¹⁵	58.8	6.1	0 ^e	0 ^e	35.1	25.0	473 K, 17 h	n.a.	3.66
Biocoal D (from bark) ¹²	70.8	6.1	0.1	0.6	21.3	30.4	523 K, 3 h	3.7	6.2
Biocoal E (from pine wood meal) ¹⁶	70.9	5.5	0.4	0.3	22.9	29.7	518 K, 20 h	n.a.	1.40
Biocoal F (from wood) ¹⁷	54.6	5.9	0.1	0 ^e	39.4	22.9	488 K, 0.5 h	n.a.	n.a.
Biocoal G (from swine manure) ¹³	68.6	7.9	2.7	0 ^e	20.8	31.8	523 K, 20 h	3.4	27.8

^a Related to the moisture- and ash-free (maf) mass. ^b All *HHV*'s in the present work were calculated according to Lloyd and Davenport¹⁸. ^c Related to the as received mass. ^d Calculated by difference. ^e Below the detection limit of 0.02 wt.-%. ^f Drying of as received coal was necessary to reach a moisture level similar to the one of as received Biocoal A (see Electronic Supplementary Information).

better biofuel properties regarding higher heating value (*HHV*) and H/C molar ratio after direct biocoal liquefaction. Except for the high ash content of Biocoal B (19.8 wt.-%), the biocoals employed in this work can be considered as superior reactants for direct liquefaction compared to biomass and lignite. As there are different types of biocoals in literature which are either produced at milder conditions (temperatures around 473 K), or more severe conditions (temperatures up to 523 K) we chose Biocoal A and Biocoal B as two extremes regarding the elemental composition and *HHV* (see Table 1) to test a wide range of biocoal liquefaction behavior. HTC residence time, the raw material and mainly the temperature are important parameters for the characteristics of the resulting biocoal^{12,13,15-17}. The higher the HTC temperature the higher the energy densification and the degree of aromaticity in the biocoal. This leads to a higher *HHV*, a higher carbon content and a lower oxygen content^{12,13,16} (see Table 1). Biocoal A is produced at milder conditions (473 K, several hours). Both, the elemental composition (see Table 1) and the *HHV* (22.6 MJ kg⁻¹) are similar to Biocoal C (25.0 MJ kg⁻¹, produced from straw at 473 K for 17 h) and Biocoal F (22.9 MJ kg⁻¹, produced from wood at 488 K for 0.5 h)^{15,17}. In contrast, Biocoal B (28.6 MJ kg⁻¹) represents the elemental composition and *HHV* of biocoals which are produced at more severe conditions like Biocoal D (30.4 MJ kg⁻¹, produced from bark at 523 K for 3 h) or Biocoal E (29.7 MJ kg⁻¹, produced from pine wood meal at 518 K for 20 h)^{12,16}. The high ash (19.8 wt.-%) and nitrogen contents (2.6 wt.-%) of Biocoal B are related to the raw material since the HTC biocoal from swine manure (Biocoal G, see Table 1) yields a similar content of ash (27.8 wt.-%) and nitrogen (2.7 wt.-%)¹³.

From a chemical point of view, it is important to use a catalyst for direct biocoal liquefaction in order to utilize gas

phase hydrogen effectively to increase the H/C molar ratio of the product by hydrogenation and to decrease the O/C molar ratio by hydrodeoxygenation. Therefore, we used an 18Ni/TiO₂ (18 wt.-% Ni related to the dry catalyst mass) catalyst whereby the nickel to maf biocoal ratio was only 1.8 wt.-%. The results of the direct liquefaction of the biocoals in 250 cm³ batch autoclave experiments are depicted in Figure 2A and could be obtained with an excellent reproducibility (± 0.3 wt.-% standard deviation). The oil yields (liquids, soluble in *n*-pentane¹⁹) were 32 and 36 wt.-% from Biocoal A and Biocoal B, respectively. From both coals, large total gas yields (C₁-C₄ hydrocarbons, water) of 58 and 45 wt.-% were obtained. The oils did neither show phase separation nor an increase in viscosity after several months of storage. The conversions were almost complete with 99 %, whereby oil, gas phase, asphaltenes (solids, soluble in toluene¹⁹) and preasphaltenes (solids, soluble in pyridine¹⁹) were considered as coal conversion products. The mass balance of ash could be closed for both biocoals.

Since the expenses for nickel (14.23 USD kg⁻¹)²⁰ are relatively high as compared to conventional, disposable catalysts for DCL based on iron²¹, catalyst recovery would be advantageous. In addition, the contact between catalyst and the macromolecular coal structure should be close, which is reached by using nanosized TiO₂ as support. Hydrogen chemisorption revealed that the average nickel particle size of the freshly activated catalyst is 170 nm. Due to the high Ni loading, the actual metal dispersion is low (0.6 %), but the catalyst shows a good activity. It should be mentioned that Biocoal A contains no detectable organic sulfur (see Table 1) which could act as a catalyst poison for the metallic nickel on titania. Thus, after Biocoal A liquefaction 99 wt.-% of the original catalyst mass of

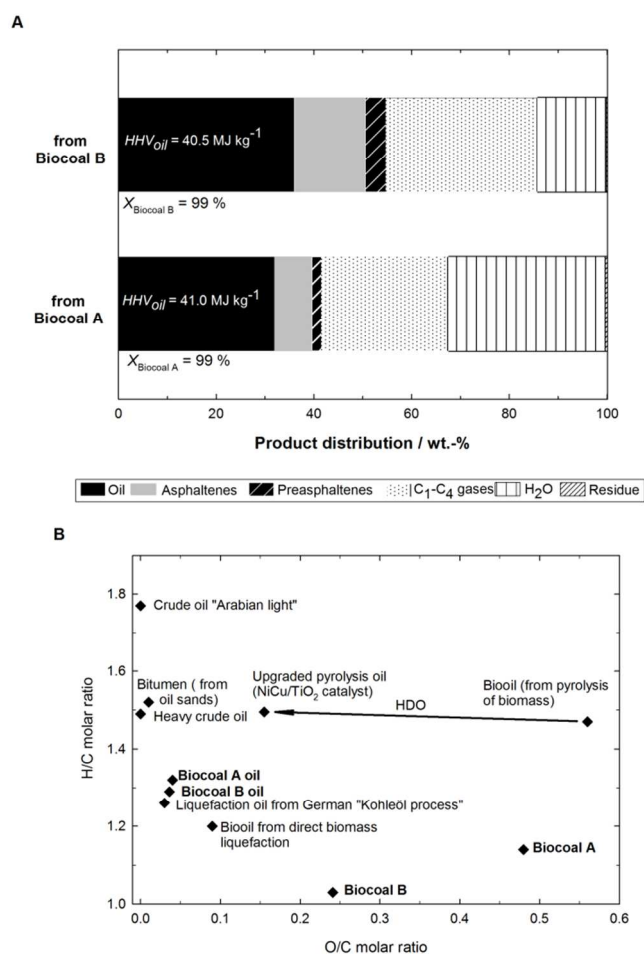


Fig. 2 Results of direct liquefaction of biocoals. **(A)** Product distribution and conversion X with $18\text{Ni}/\text{TiO}_2$ catalyst. Catalyst amount: 10 wt.-% related to maf biocoal; $T_{\text{reaction}} = 673\text{ K}$; $t_{\text{reaction}} = 2\text{ h}$; $p_{\text{hydrogen, cold}} = 10\text{ MPa}$; $m_{\text{metal}}/m_{\text{maf biocoal}} = 5$. Reproducibility = $\pm 0.3\text{ wt.-%}$ (standard deviation). HHV s were calculated according to Lloyd and Davenport¹⁸. **(B)** Van Krevelen diagram with biooils obtained by different routes and fossil oils²³⁻²⁷.

the ferromagnetic $18\text{Ni}/\text{TiO}_2$ could be recovered by magnetic gradient in its original form. The nickel particle size of the reactivated catalyst is 1300 nm and the dispersion is 0.07 % which is clearly owed to metal sintering during the reaction and the recovery procedure. The main products were analyzed with regard to Ni contents. Oil, asphaltenes and preasphaltenes contained 0.01, 0.03 and 0.4 wt.-% of Ni, respectively. Thus, only 0.7 wt.-% of the Ni were leached out from the catalyst. Direct Biocoal A liquefaction with the reactivated catalyst showed a drop in oil yield to 26 wt.-%. The conversion rose by one percent but this is within experimental error. For liquefaction reactions with Biocoal B, the catalyst could only be recovered by < 25 wt.-% which is due to the small sulfur amounts in Biocoal B (0.2 wt.-%). Due to the sulfidation of $18\text{Ni}/\text{TiO}_2$, the ferromagnetic properties of the catalyst were lost. Hence, an alternative concept should be considered for the case that the biocoal contains organic sulfur. One possibility could be fumed metal oxide nanoparticles as a support, which encapsulate a magnetic component like Fe_3O_4 . Such $\text{Fe}_3\text{O}_4@/\text{TiO}_2$ nanoparticles have already been synthesized by Y. Li et al²².

For an evaluation of the different routes for the production of biofuels, the H/C and O/C molar ratios of several substances are

illustrated in a Van Krevelen Diagram (Figure 2B). The H/C (1.29 for Biocoal B oil, 1.32 for Biocoal A oil) and O/C molar ratios (0.04 for Biocoal B oil and for Biocoal A oil) of our oils could not reach the values of fossil fuels such as bitumen from oil sands, heavy crude oil or light crude oil, but the values are better than those of a direct coal liquefaction oil from the German "Kohleöl process" and of biooil from direct biomass liquefaction²³⁻²⁷. Only oils obtained by fast pyrolysis of biomass and upgraded by hydrodeoxygenation (HDO) have a higher H/C molar ratio (1.50)²⁵. However, the oxygen content of these oils is significantly higher, and this causes a lower HHV . In order to get an insight into the chemistry of the direct biocoal liquefaction, Fig. 3 shows that for Biocoals A and B, the structural functionalities are similar. The broad region around 3316 cm^{-1} partly results from moisture and hydroxyl groups^{28,29}. There are weak signals around $3000\text{-}2800\text{ cm}^{-1}$ indicating aliphatic C-H stretching³⁰. Around 1700 cm^{-1} , C=O stretching vibration frequencies can be found. The biocoals also show aromatic skeletal vibrations at 1600 cm^{-1} ³⁰. The strong signals at 1030 cm^{-1} arise from a high abundance of primary alcohols and can be confirmed by the O-H stretching around 3316 cm^{-1} and the high oxygen content of the coals. Furthermore, the shoulders around 1100 cm^{-1} show aliphatic ether bonds³⁰. The extracted oils show a significant decrease in the C-O stretching modes from $1030\text{-}1100\text{ cm}^{-1}$ which is confluent with the decrease of the O/C molar ratio of the oils (see Figure 2B) in contrast to the coal which is caused by catalytic hydrodeoxygenation (HDO) through a catalytic C-O-bond hydrogenolysis. The increasing H/C molar ratio (Figure 2B) of the liquids is reflected by the increase in intensity of C-H stretching modes at $3000\text{-}2800\text{ cm}^{-1}$ through the

Ni-catalyzed hydrogenation. Mechanistic insights could be obtained by reactions of the coal-related model compound ethoxybenzene (for details see Electronic Supplementary Information) revealing that the $18\text{Ni}/\text{TiO}_2$ catalyst is able to cleave more stable $\text{C}_{\text{aromatic}}\text{-O}$ bonds by hydrogenolysis (for HDO) and to hydrogenate aromatic rings in contrast to the noncatalytic liquefaction where only thermal and solvent-induced reactions take place. This explains the much lower conversion (78 %) and oil yield (17 wt.-%) for the noncatalytic Biocoal A liquefaction with an oil having a lower molar H/C ratio (1.16) and more oxygen (7 wt.-%) which leads to a lower HHV_{oil} of only 39.5 MJ kg^{-1} . Additionally, through the acidic centers on TiO_2 many small fragments can be transalkylated and are not released into the $\text{C}_1\text{-C}_4$ gas phase (hydrocarbon gas yield = 37 wt.-% for the noncatalytic reaction, 26 wt.-% for the catalytic reaction).

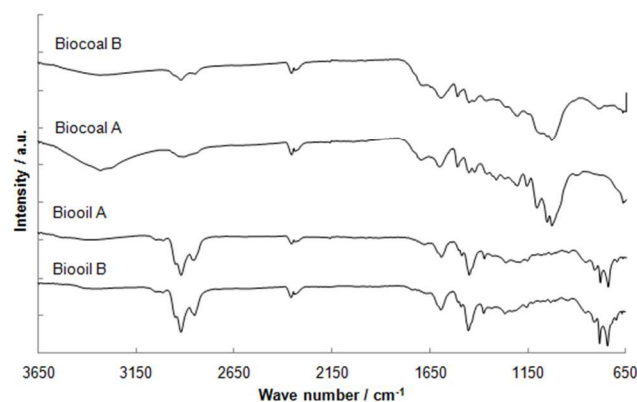


Fig. 3 ATR spectra of Biocoals A and B and the extracted oils.

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Table 2 Characteristics required for a bio-petroleum according to Wang *et al.*³¹. Biooils from pyrolysis + HDO, direct biomass liquefaction and direct biocoal liquefaction oils are discussed ((X) = criterion not fulfilled, (✓) = criterion fulfilled).

	Standard ³¹	Biomass liquefaction oil ²³	Pyrolysis + HDO Upgraded oil ^{25, a}	Biocoal liquefaction oils (this work)	
Experimental conditions		653 K, 0.25 h, 1.6 MPa H ₂ , 20 wt.-% Raney-Ni, $m_{\text{tetralin}}/m_{\text{biomass}} = 14$	623 K, 3h, 11.1 MPa H ₂ , 20 wt.-% 9.1Ni-3.1Cu/TiO ₂	Biocoal B 673 K, 2 h, 10 MPa H ₂ , 10 wt.-% 18Ni/TiO ₂	Biocoal A 673 K, 2 h, 10 MPa H ₂ , 10 wt.-% 18Ni/TiO ₂
				$m_{\text{tetralin}}/m_{\text{maf biocoal}} = 5^b$	$m_{\text{tetralin}}/m_{\text{maf biocoal}} = 5^b$
H/C molar ratio	> 1.5	1.20 (X)	1.5 (✓)	1.29 (X)	1.32 (X)
HHV ^c / MJ kg ⁻¹	> 40.0	38.3 (X)	35.2 (X)	40.5 (✓)	41.0 (✓)
w _o ^d / wt.-%	< 6.0	10.0 (X)	15.1 (X)	4.1 (✓)	4.6 (✓)

^a Experimental conditions of the HDO step are given. ^b Polycyclic aromatic hydrocarbons like tetralin are important for the liquefaction mechanism. In practical applications, tetralin will be recycled and after a few reaction cycles heavy biocoal liquids can replace tetralin and its function ^c HHV calculated according to Lloyd and Davenport¹⁸. ^d All oxygen contents are calculated by difference.

According to Wang *et al.*, the key point to convert biomass into useful petroleum-like oil is to remove enough oxygen. They established a new standard for so-called bio-petroleum which should fulfill several characteristics, namely, an H/C molar ratio > 1.5, an HHV > 40.0 MJ kg⁻¹ and an oxygen content < 6.0 wt.-%³¹. In Table 2, oils from direct liquefaction of biomass, direct liquefaction of biocoal and HDO of pyrolysis oils are compared with regard to the mentioned bio-petroleum standard³¹. Oils from direct biomass liquefaction do not fulfill even one of the mentioned quality criteria. Hydrotreated pyrolysis oils have an H/C molar ratio of 1.5 but a far too low HHV of 35.2 MJ kg⁻¹ and a too high oxygen content of 15.1 wt.-%. Each of our oils produced from direct biocoal liquefaction fulfills two out of three criteria. They are superior in HHV (40.5 MJ kg⁻¹ for Biocoal B and 41.0 MJ kg⁻¹ for Biocoal A) to the other oils compared in Table 2. The oxygen contents of Biocoal B oil (4.1 wt.-%) and Biocoal A oil (4.6 wt.-%) are clearly the only oils which meet the required standard of < 6 wt.-%. The only criterion which was not fulfilled is the H/C molar ratio of > 1.50; here, the upgraded pyrolysis oil is superior. Hence, this discussion shows that the three different routes to biofuels are complementary. One should also take into account that oils from direct biomass liquefaction can be upgraded further and that our alternative concept comprises only one stage of biocoal liquefaction. Many direct liquefaction concepts of fossil coal consider two stages²¹.

Conclusions

Altogether, we present an alternative concept for the production of second-generation biofuels consisting of biomass conversion by hydrothermal carbonization with subsequent direct liquefaction of the biocoal thus obtained. This concept provides an economic solution for the logistic problems caused by the high moisture contents of biomass. If the sulfur content in biocoal is zero which is possible by controlled HTC, 99 wt.-% of our

catalyst could be recovered by magnetic gradient. The produced biofuels are of good quality and almost reach the standard of bio-petroleum³¹. Our alternative route is a carbon dioxide neutral perspective for the production of second-generation biofuels and deserves further evaluation. Biocoals similar to Biocoal A are well suited for fuel production by direct liquefaction whereas biocoals similar to Biocoal B with high nitrogen and ash contents are more appropriate for soil amendment.

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- † Electronic Supplementary Information (ESI) available: [catalyst characterizations; coal and oil analytics; coal-related model compound reactions; direct liquefaction procedure]. See DOI: 10.1039/b000000x/
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