BioMates

Public Summary of Deliverable D 1.5:

Report on evaluation of by-product utilisation pathways

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Contents

1. Preface

Permanent gases and char are by-products of every pyrolysis process aiming at liquid condensates as main product. For BioMates ablative fast pyrolysis, routes to make use of these by-products should be identified. The basic idea behind it is to optimise the by-products' contribution to the overall revenue and the positive sustainability effects of using residuals- and grass-biomass for fuel production.

In the case of pyrolysis char (alternatively named pyrolysis coke), the application as solid fuel for industrial processes is an obvious route that makes the heating value define the monetary threshold for each alternative application. This deliverable focusses on potentially more economic application alternatives.

2. Introducing BioMates

2.1. The BioMates Project

The BioMates project aspires in combining innovative 2nd generation biomass conversion technologies for the cost-effective production of *bio*-based inter*mediates* (BioMates) that can be further upgraded in existing oil refineries as renewable and reliable co-feedstocks. The resulting approach will allow minimisation of fossil energy requirements and therefore operating expense, minimization of capital expense as it will partially rely on underlying refinery conversion capacity, and increased bio-content of final transportation fuels.

The BioMates approach encompasses innovative non-food/non-feed biomass conversion technologies, including **ablative fast pyrolysis (AFP)** and single-stage **mild catalytic hydroprocessing (mild-HDT)** as main processes. Fast pyrolysis in-line-catalysis and fine-tuning of BioMates-properties are additional innovative steps that improve the conversion efficiency and cost of BioMates technology, as well as its quality, reliability and competitiveness. Incorporating **electrochemical H_2-compression** and the state-of-the-art **renewable H_2-production** technology as well as **optimal energy integration** completes the sustainable technical approach leading to improved sustainability and decreased fossil energy dependency. The overall BioMates-Concept is illustrated in Figure 1.

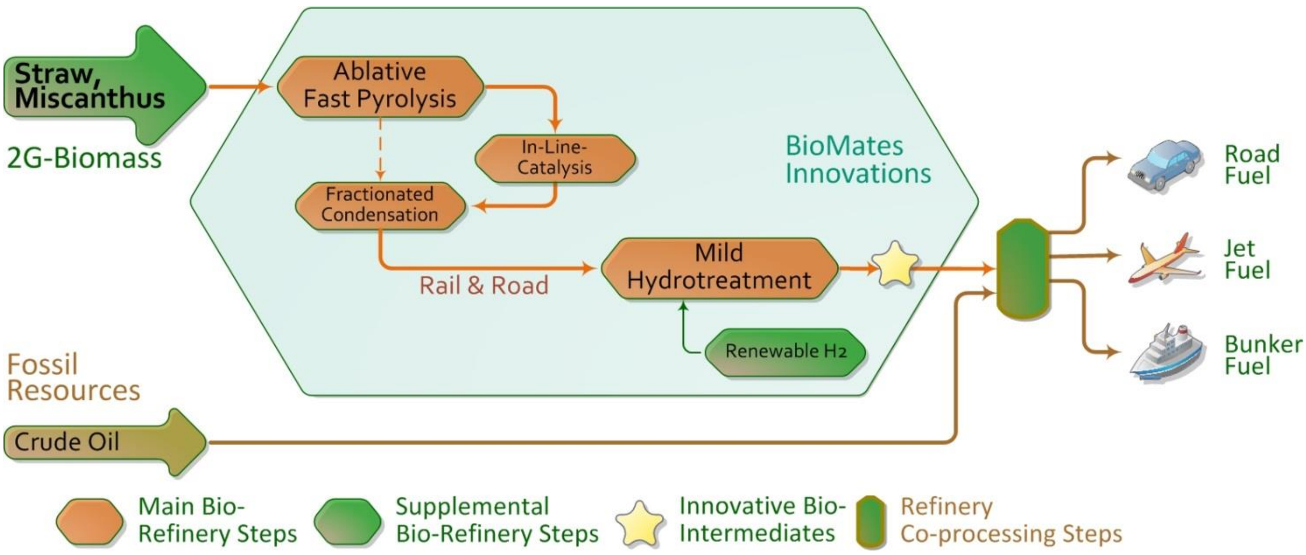

Figure 1: The BioMates-concept

The proposed technology aims to effectively convert residues and non-food/feed plants or commonly referred to as 2nd Generation (straw and short rotating coppice like miscanthus) biomass into high-quality bio-based intermediates (BioMates), of compatible characteristics with conventional refinery conversion units, allowing their direct and risk-free integration to any refinery towards the production of hybrid fuels.

2.2. European Commission support

The current framework strategy for a Resilient Energy European Union demands energy security and solidarity, a decarbonized economy and a fully-integrated and competitive pan-European energy market, intending to meet the ambitious 2020 and 2030 energy and climate targets /EC-2014a, EC-2014b/. Towards this goal, the European Commission is supporting the BioMates project for validating the proposed innovative technological pathway, in line with the objectives of the LCE-08-2016-2017 call /EC-2015/. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727463.

2.3. The BioMates team

The BioMates team comprises eight partners from industry, academia and research centres:

- Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Germany (Project Coordination) - *www.umsicht.fraunhofer.de*
- Centre for Research & Technology Hellas / CERTH - Chemical Process & Energy Resources Institute / CPERI, Greece - *http://www.cperi.certh.gr/*
- University of Chemistry and Technology Prague, Czech Republic - *http://www.vscht.cz*
- Imperial College London, United Kingdom
  www.imperial.ac.uk
- Institut für Energie und Umweltforschung Heidelberg GmbH / ifeu, Germany - *www.ifeu.de*
- HyET Hydrogen B.V. / HyET, Netherlands - *www.hyethydrogen.com*
- RANIDO, s.r.o., Czech Republic
  http://www.ranido.cz/
- BP Europa SE, Germany
  www.bp.com/en/bp-europa-se.html

For additional information and contact details, please visit *www.biomates.eu*.

3. Utilisation of pyrolysis char

3.1. Activated carbon production

Biomass-based fast pyrolysis chars usually exhibit rudimentary porous systems. The main characteristic parameter for adsorbents' porous systems is the mass-related specific surface, usually derived from N_2–isotherms according to the evaluation-method of Brunauer, Emmett and Teller ("BET-surface") /Brunauer-1938/. The BET surface areas of fast pyrolysis chars usually range from < 5 m^2g^{-1} to 33 m^2g^{-1}, which keeps them far away from activated carbons that that start with specific surfaces of about 500 m^2g^{-1} /Azargohar-2013/Fu-2012/Wingender-2011/.

Like many other carbon materials, pyrolysis coke can be processed by gas activation at ambient pressure with CO_2 at ≈ 800 °C or H_2O at ≈ 900 °C. In this process, carbon is removed from the solid as CO or CO_2. Typically, a carbonisation (temperature treatment under inert gas) precedes activation in order to remove volatile components /von Kienle-2018/.

While a fraction of the activated carbon precursor's C-content leaves the matrix to form a meso- and micropore system, the ash content remains unharmed, dominating the weight ratios more and more with raising activation grade, but contributing nothing to the specific surface ("Burn-off"-effect). Therefore, a low ash content is a vital parameter for a promising activated carbon precursor.

Typically, the ash content qualifies rather wood than straw-like biomass for processing its pyrolysis ashes to activated carbon. For selected plants of Irish origin, Butler et al. reported moisture-free (mf) ash content to increase in the order spruce (0.26 wt.%^{mf}) < salix[1] (1.16 wt.%^{mf}) < miscanthus (3.43 wt.%^{mf}) < wheat straw (3.76 wt.%^{mf}) /Butler-2013/.

Carbonising and thereafter activating spruce-whitewood-derived fast-pyrolysis char (char ash content: 13.6 wt.%^{mf}) towards activated carbon is described in literature to lead to encouraging results. Azargohar et al. achieved BET surfaces of 643 m^2g^{-1} via steam activation and 783 m^2g^{-1} via chemical activation with KOH, and Dehkhoda et al. even received up to 2,673 m^2g^{-1} BET surface area by applying chemical activation with KOH /Azargohar-2008/Dehkhoda-2016/. However, due to the described differences in ash content, these encouraging results cannot be directly transferred to processing straw-based material.

Compared to the straw-like materials mentioned above, the feedstock materials applied within BioMates show a slightly lower ash content, but with 3.1 wt.%^{mf} for wheat / barley straw and 2.5 wt.%^{mf} for Miscanthus (see Table 1), they still bear more than twice the ash content than the reported salix wood, for example /BioMates-D1.4/.

The ash content of solids in the BioMates AFP process is given in Table 1. Here, the ash content is given for the overall pyrolysis char (fine and coarse fractions).

Table 1: Ash content of solids in the AFP process /BioMates-D1.4/

Ash content wt.%^{mf} [1]	Wheat / barley straw	Miscanthus
Feedstock	3.1	2.5
Overall pyrolysis char	11.0	7.3
[1] ^{mf}: moisture-free basis		

For reference: a typical commercial, steam-activated, coconut-based granular activated carbon with a BET-surface around 1,100 m^2g^{-1} may have an ash content of 5 % max (corresponding with a carbon content of about 95 wt.-%) /Silcarbon-2006/.

As carbonisation and subsequent activation would considerably increase the presented ash contents of 11.0 wt.%^{mf} (ash from wheat/barley straw) and 7.3 wt.%^{mf} (ash from Miscanthus), any produced material would miss said carbon content of typically about 95 wt.-% required for high-grade activated carbons by far.

Consequently, it can be stated that the AFP-chars from the BioMates feedstock materials can hardly be expected to yield high-quality activated carbons – there are simply lots of other base materials that are more suited for this task. Ash-removal upfront the activation would be technically feasible, but economically pointless.

On the other hand, the char could possibly serve for interesting catalytic properties of the generated activated carbons, even if they could never gain high adsorbent qualities. Therefore, applying AFP-char-derived activated carbon as alternative catalyst for AFP in-line-catalysis could possibly turn out to be advantageous –

[1] Short rotation coppice willow

the more as it would possibly avoid purchasing catalysts in later commercial applications of the BioMates process concept.

3.2. Agricultural applications - Biochar

3.2.1. Biochar – Nature and Definition

Using pyrolysis coke for agricultural applications is state of technology. In this context, biomass-based pyrolysis coke is called *"Biochar"*. The Switzerland-based *European Biochar Foundation* issues and constantly updates the *European Biochar Certificate* (EBC), a voluntary European industrial standard for Biochar with sustainable production and low hazard use in agronomic systems. This certificate defines Biochar as follows /EBF-2018/:

> "Biochar is a heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of sustainably obtained biomass under controlled conditions with clean technology and is used for any purpose that does not involve its rapid mineralisation to CO_2 and may eventually become a soil amendment.
>
> Biochar is produced by biomass pyrolysis, a process whereby organic substances are broken down at temperatures ranging from 350 °C to 1000 °C in a low-oxygen thermal process. Torrefaction, hydrothermal carbonisation and coke production are further carbonisation processes whose end products cannot however be called biochar under the above definition. Biochars are therefore specific pyrolysis chars characterised by their additional environmentally sustainable production, quality and usage features. […]
>
> In accordance with the certificate to which these guidelines apply, a differentiation is made between two different biochar grades, each with its own threshold values and ecological requirements: "basic" and "premium". […]"

Furthermore, the EBC defines some requirements regarding the feedstock. Besides the absence of non-organic wastes and contaminants as well as special requirements for woody biomass, these requirements are /EBF-2018/

> "3.1 Only organic wastes listed in the positive list (Appendix 1) may be used in the production of biochar.
>
> 3.4 When using primary agricultural products, it must be guaranteed that these were grown in a sustainable manner.
>
> 3.6 Feedstocks used for the production of biochar must not be transported over distances greater than 80 km. [...]
>
> 3.7 Complete records of feedstocks must be kept."

The corresponding *"Positive list of biomass feedstock approved for use in producing Biochar"* contains *"Straw, used straw, husks and grain dust"* with the comment "Attention: health & safety precautions where dust is involved - Only waste not / no longer usable for human consumption or as animal feed" /EBF-2013/.

All these requirements are met or – with regard to the feedstock – can be easily met in later industrial application of BioMates, especially when the concept of decentralised, optionally mobile AFP-plans will be put into practice.

3.2.2. Indicative fertiliser performance test

In order to evaluate the applicability of BioMates AFP pyrolysis coke (BioMates PyCoke) as Biochar, indicative fertiliser performance tests were performed, involving lettuce and wheat as trial species. Coarse char, derived in the hot gas filter of the TRL4-AFP-plant from wheat/barley straw like described in Chapter 4 of Deliverable 1.4, was used as BioMates PyCoke /BioMates-D1.4/.

Reference soil ("Floraself peat-free cultivation soil" /Hornbach-2018/) was used applied and as mixture with addition of 2.5, 5.0 and 7.5 w.t-% PyCoke (coarse char, derived in in the BioMates TRL4-AFP-plant from wheat/barley straw). Lettuce and wheat were grown in seed boxes on these soil samples (3 parallel samples each). The maximum height of the plants in each box was measured. Exemplarily, the set-up further growth is documented with pictures of day 29 (days are always counted as "days after planting") in Figure 2. On day 45, the plants were harvested.

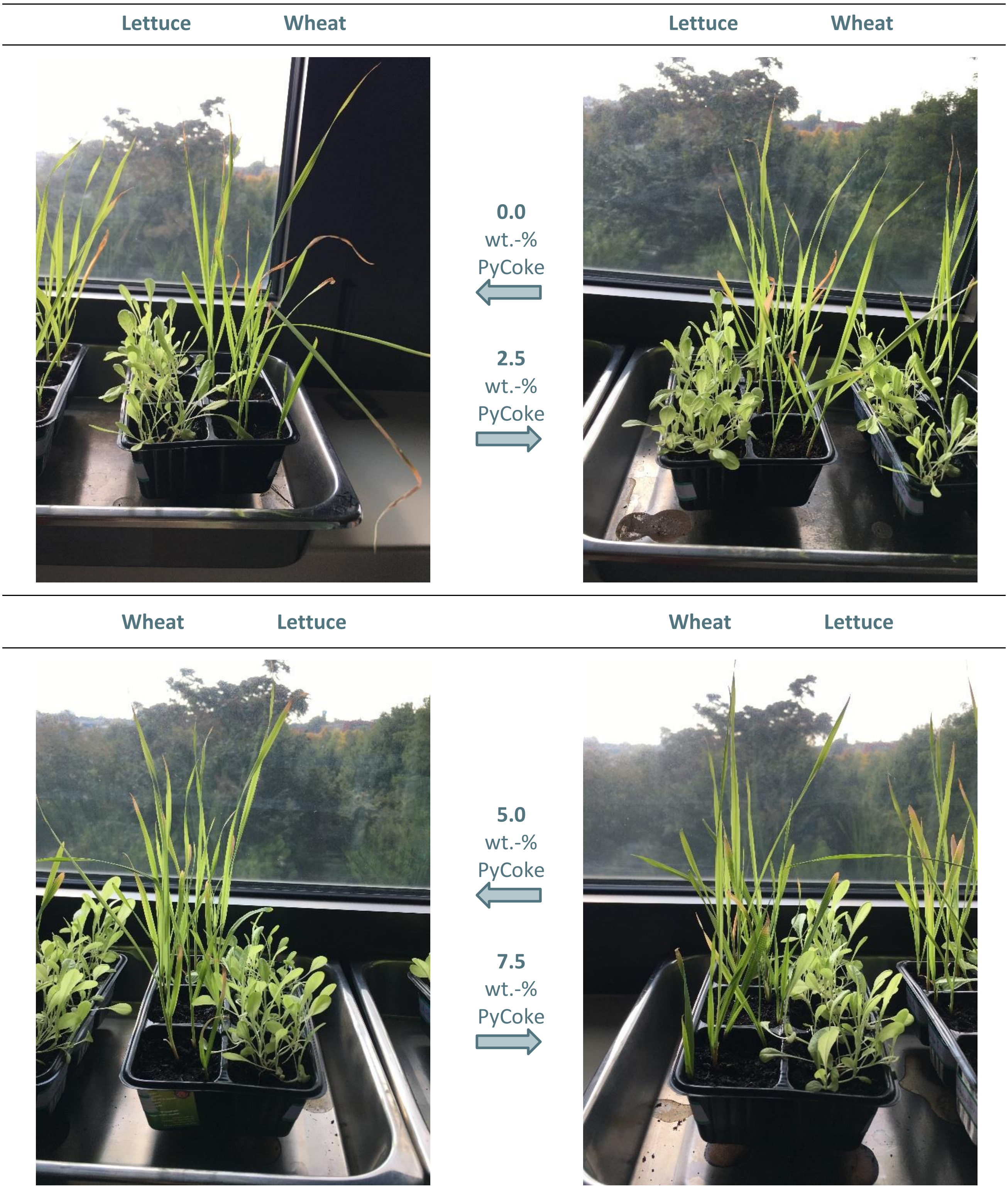

Figure 2: Fertiliser performance test: seed boxes with lettuce and wheat on day 29

Measuring the height of the plants over the experimental time lead scarcely to significant results. But in the harvested lettuce seedlings, the above-ground, green parts of the plant got less dense, while the rootage became larger and denser with rising PyCoke content. Furthermore, with increasing PyCoke content in the soil, the rootage contained more water. Quite in contrast, for wheat, the above-ground, green parts of the plant as well as the rootage diminished with rising PyCoke content.

3.2.3. PAH content

In order to compare the AFP-coke's content of polycyclic aromatic hydrocarbons (PAHs) to the EBC-standard, coke from the BioMates AFP-plants was chemically analysed. In addition to coke from the TRL4-AFP-plant used within WP1, coke from the TRL5-AFP-plant (the one that will be upgraded and used in WP3) was included in the test series.

The coke has been taken from the reactor (coarse char) and the hot gas filter - HGF (fine char) in TRL4. In the TRL5-plant, the coke was derived from within the reactor and from the cyclone. As feedstock, Miscanthus and wheat/barley straw like described in Chapter 4 of Deliverable 1.4 were used /BioMates-D1.4/.

The coke samples were analysed for polyaromatic hydrocarbons (PAH) via extraction with toluene, followed by GC-MS, resembling the method defined in the European Biochar Certificate (EBC) /EBF-2018/. The content of the usual set of 16 individual PAHs was determined, each of them with a detection limit of 0.1 mg kg^{-1} dry matter (DM). Summing up the determined contents lead to 0.80 - 2.63 mg kg^{-1} DM for the six samples, which defines the minimum PAH content. For the maximum PAH content, the sum of detection limits for all non-detected individual substances have to be added, what lead to values of 1.70, 1.80, 2.10, 2.41, 3.24 and 3.43 mg kg^{-1} DM.

For a Biochar's PAH content, the *European Biochar Certificate* demands /EBF-2018/:

> "6.8 The biochar's PAH content (sum of the EPA's 16 priority pollutants) must be under 12 mg kg^{-1} DM [dry matter] for basic grade and under 4 mg kg^{-1} DM for premium grade biochar."

Consequently, concerning the PAH content, all samples met the EHC-requirements for premium-grade biochar (where it has to be repeated that the applied method varied very slightly from the one defined in the EBC).

3.2.4. Heavy metals content

For a Biochar's heavy metals content, the *European Biochar Certificate* demands /EBF-2018/:

> "6.6 The following thresholds [referring to the biochar's total dry mass (DM)] for heavy metals must be kept [..]:
> basic: Pb < 150 g t^{-1} DM; Cd < 1,5 g t^{-1}DM; Cu < 100 g t^{-1} DM; Ni < 50 g t^{-1} DM; Hg < 1 g t^{-1} DM; Zn < 400 g t^{-1} DM; Cr < 90 g t^{-1} DM; As < 13 g t^{-1} TM
> premium: Pb < 120 g t^{-1} DM; Cd < 1 g t^{-1} DM; Cu < 100 g t^{-1} DM; Ni < 30 g t^{-1} DM; Hg < 1 g t^{-1} DM; Zn < 400 g t^{-1} DM; Cr < 80 g t^{-1} DM; As < 13 g t^{-1} TM
> […]"

The BioMates chars described in the above section 3.2.3 were analysed for six of the eight heavy metals of said EHC's list. Table 2 compares the maximum- and minimum-results of all samples for each determined heavy metal to the EHC's requirements.

Table 2: Heavy metal analysis of 6 BioMates coke samples, compared to the EHC requirements /EBF-2018/

Requirement / result	EHC		BioMates samples	
	Basic	Premium	Minimum	Maximum
Heavy Metal	Concentration (g t^{-1} dry matter)			
Pb	< 150	< 120	< 2	< 2
Cd	< 1.5	< 1.0	< 0.2	< 0.2
Cu	< 100	< 100	8.78	31.8
Ni	< 50	< 30	2.69	28.8
Zn	< 400	< 400	58.8	180
As	< 13	< 13	< 1	< 1

For all six measured heavy metals, the measured contents underscore the limits for EHC premium Biochar by far.

4. Utilisation of permanent gas

The permanent gases remaining after the condensation train of BioMates AFP were analysed for O_2, H_2, CH_4, CO and CO_2 content, partly additionally for the content of higher hydrocarbons (C_{2+}). The energy content calculated from the derived results qualifies the gaseous AFP by-product for supplying the heating energy for the AFP reactor, thus replacing the electricity applied in the TRL4-APF-plant. As this application would completely consume the permanent gases inside the process for heating purposes, no external exploitation options were considered.

5. Conclusions and outlook

Using BioMates-chars as base material for high-quality activated carbons does not seem to be too promising.

The indicative fertiliser performance tests suggest that BioMates PyCoke could enhance the rootage growth for lettuce but may be contra-productive for wheat. Further tests with standard soil from typical agriculturally-used fields as reference soil should be conducted in co-operation with bio-science specialists later on.

Concerning the PAH content and the content of the six analysed heavy metals, all six char samples, covering the whole range of feedstock materials and pyrolysis plants to be used within BioMates, meet the EHC-requirements for premium-grade biochar. This result definitely indicates the use of BioMates-derived pyrolysis coke as Biochar as an option to be pursued.

The permanent gas can be used to provide heat for the AFP process.

6. Disclaimer

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