Journal of Cleaner Production 130 (2016) 58–67

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

A comparison between microalgae virtual biorefinery arrangements for bio-oil production based on lab-scale results

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ARTICLE INFO

Article history:
Received 13 April 2015
Received in revised form
30 June 2015
Accepted 13 September 2015
Available online 25 September 2015

Keywords:
Bioenergy
Microalgae
Solvent extraction
Pyrolysis
Bio-oil

ABSTRACT

Bio-oils are typically produced by pyrolysis processes. Bio-oils can be used directly in a generator to produce electricity or upgraded to produce transportation fuels. Nowadays the interest is that they come out in a biorefinery context. This paper compares bio-oil production within three possible procedures. Targeting the bio-oil product, in virtual biorefinery #1, microalgae is processed by solvent ultrasound-assisted extraction, and lipids follow transesterification; in virtual biorefinery #2, bio-oil comes out from fresh microalgae pyrolysis, and, finally, in virtual biorefinery #3, lipid extraction leftovers proceed for slow pyrolysis. Solvent ultrasound-assisted extraction and slow pyrolysis are tested and measured experimentally using three microalgae as feedstock: *Chlorella vulgaris*, *Nannochloropsis oculata*, and *Scenedesmus obliquus*. These stand-alone processes are analyzed aiming to provide the best option in a virtual biorefinery context. Although very fast/slow pyrolysis produces markedly different products, previous thermogravimetry analysis allowed choosing an adequate pyrolysis temperature. Nevertheless, the influence of temperature, catalyst and nitrogen flow is depicted. The comparison indicators for final remarks relate to final energy consumption and greenhouse gas emissions. Conditions that favor bio-oil production may not be favorable in terms of energy required per mass or energy output. If mass allocation criterion is used lipid extraction followed by slow pyrolysis of the leftovers is advantageous over slow pyrolysis of fresh dry microalgae. Still the fossil energy input largely surpasses the bio-oil energy content.

1. Introduction

The conversion of microalgae biomass to biofuels and added value products are globally gaining significant prominence and there has been an increased focus on this research area over the last few years (Liew et al., 2014). Microalgal contain high levels of oils, carbohydrates and proteins which make them versatile raw materials for fuels production in parallel with valuable chemicals and human and animal food in a biorefinery context. Bio-oils are typically produced by disruption or pyrolysis processes, where the biomass is heated in the absence of oxygen. The bio-oils can be used directly in a generator to produce electricity or upgraded to produce transportation fuels.

Lee et al. (2012) provides an overview of microalgal cell disruption processes which are potentially suitable for large scale lipid extractions. The energy requirements of these processes were compared with each other and then compared with estimates of the theoretical minimum energy required for disruption. Fig. 1 shows the typical disruption methods that can be used *per si* or combined with each other. A range of 9.6–529 MJ/$kg_{dry\ microalgae}$ is reported for the final energy consumption, covering different microalgae and different methods.

Three different thermochemical conversion routes are found according to the oxygen content in the process: combustion (complete oxidation), gasification (partial oxidation) and pyrolysis (thermal degradation without oxygen). The last one is used for bio-oil production.

Pyrolysis is a promising bioconversion technique for energy recovery, waste management, and converting biomass into useful energy products that has attracted considerable attention during the past decades due to its bioenergy production capability (Liew et al., 2014).

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http://dx.doi.org/10.1016/j.jclepro.2015.09.053
0959-6526/

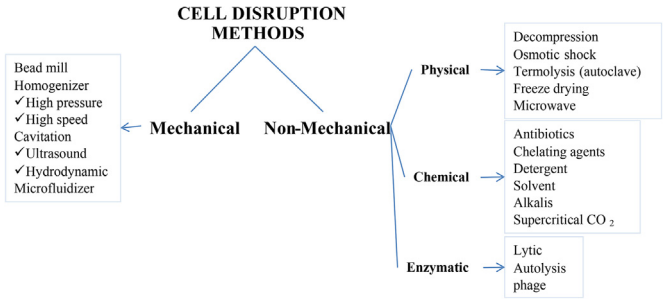

Fig. 1. Classification of cell disruption methods (adapted from Lee et al. (2012)).

Within a pyrolysis process the raw material is converted into different reactive intermediate products: solid (bio-char), liquid bio-oils (heavy molecular weight compounds that condense when cooled down) and gaseous products (low molecular weight gases) (Fernández et al., 2011).

The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstock. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of char. Short residence time pyrolysis (fast, flash, rapid) of biomass at moderate temperatures has generally been used to obtain high yield of liquid products (Yaman, 2004).

Depending on the pyrolysis temperature, the char fraction contains inorganic materials ashed to varying degrees, any unconverted organic solid and carbonaceous residues produced from thermal decomposition of the organic components. Bio-char offers numerous benefits when applied to soils and it potentially delivers a net reduction of atmospheric carbon dioxide, achieved across the combined cultivation and processing regime overall as a function of time (Grierson et al., 2011). The oil fraction is a complex mixture of organic chemicals. The pyrolysis technology can be classified as seen in Table 1.

Recent studies were developed using microwave assisted pyrolysis. Conventional heating pyrolysis (CP) is different than microwave assisted pyrolysis (MP) in the material heating process. In MP the heating material is at higher temperature than the surrounding area, unlike conventional heating where it is necessary that the conventional furnace cavity reach the operating temperature, to begin heating the material (Shuttleworth et al., 2012).

The energy and emissions data inventory is relevant for comparing processes (Castanheira et al., 2015), improving a process itself (Pérez-López et al., 2014) or consider it sustainable. For example, Renewable Energy Directive 2009/28/EC (RED) consider that biofuels must achieve life cycle greenhouse gas savings of at least 35% in comparison to fossil fuels. This savings requirement rises to 50% in 2017. In 2018, it rises again to 60% but only for new production plants.

Zhong et al. (2010) reported the life-cycle assessment of flash pyrolysis of wood waste. The authors showed that the process of flash pyrolysis of wood waste is in fact environmentally friendly.

Table 1
Pyrolysis technology classification (Fernández et al., 2011).

Residence time (s)	Heating rate (K/s)	Temperature (K)	Classification
450–550	0.1–1	550–950	Slow
0.5–10	10–200	850–1250	Fast
<0.5	>1000	1050–1300	Flash

Steele et al. (2012) reported bio-oil feedstock produced using whole southern pine (*Pinus taeda*) trees, chipped, and converted into bio-oil by fast pyrolysis (in CP category, with conditions: Fluidized bed pyrolysis feed, 500 °C, 2.75 kg air/kg, 59% bio-oil yield). It indicates 1.39 $MJ/MJ_{bio\text{-}oil}$ primary energy consumption and 0.04 kg $CO_2/MJ_{bio\text{-}oil}$ for bio-oil production stage. Khoo et al. (2013) reported lipid extraction and bio-oil production by fast pyrolysis (in CP category, with a fixed-bed reactor, 550 °C, nitrogen flow rate of 650 mL/min and a yield of 15.4 wt.% bio-oil) using the microalgae *Nannochloropsis* sp. It considers lipid extraction with solvent (85.7 $MJ/kg_{dry\ microalgae}$) followed by fast pyrolysis to obtain bio-oil. For the lipid depleted biomass feedstock, the energy input for the CP is 0.17 $MJ/MJ_{bio\text{-}oil}$ and the CO_2 emissions for the CP is 0.38 kg $CO_2/MJ_{bio\text{-}oil}$. Wang et al. (2015) investigated if a pyrolysis refinery using municipal solid waste (MSW) would be environmentally friendly using the life cycle assessment methodology. Authors conclude that the refinery of each kg MSW requires 4.71 MJ from which 71.3% are due to fast pyrolysis.

Xu et al. (2011) reported lipid extraction and bio-oil production by fast pyrolysis (in CP category, conditions: transesterification and pyrolysis for 70 wt.% bio-oil yield) using the microalgae *Chlorella vulgaris*. It considers lipid extraction by cell disruption by a stirred ball mill and solvent extraction (final energy consumption of 0.24 $MJ/kg_{dry\ microalgae}$), followed by fast pyrolysis to obtain bio-oil (final energy consumption of 0.06 $MJ/MJ_{bio\text{-}oil}$).

Du et al. (2011) reported microwave-assisted pyrolysis of microalgae *Chlorella* sp. for biofuel production. No energy or emissions balance information was reported which makes impossible a comparison among processes.

Araujo et al. (2013) reported an ultrasound-assisted extraction. The authors verified that sonication increased the efficiency of the extraction since it was partially responsible for cell disruption. Prommuak et al. (2012) examined solvent extraction of lipid from microalgae, *H. pluvialis* and *C. vulgaris* assisted by microwave. No energy or emissions balance information was reported which makes impossible a comparison among processes.

Catalyzed pyrolysis of biomass over ZSM-5 catalysts was previously reported by several researchers (Bulushev and Ross, 2011). Pan et al. (2010) studied the catalyzed and non-catalyzed pyrolysis of *Nannochloropsis* sp. in a tubular fixed bed reactor under N_2 flow. They used different amounts of HZSM-5. The authors reported lower oxygen content for bio-oils obtained by catalyzed pyrolysis, 19.5 wt.% instead 30.1 wt.%, and higher heating-value 32.7 MJ/kg instead 24.6 MJ/kg (Lappas, 2002) compared the catalytic performances of ZSM-5, quartz sand and a commercial FCC catalyst during the biomass pyrolysis in a circulating bed reactor. Basic catalysts, such as alkaline and alkaline earths carbonates, are also referred to be active for biomass pyrolysis e.g.: Zhang et al. (2008) studied the effect of additives (Na_2CO_3, NaOH) on the pyrolysis of waste rubber; The effects of basic catalysts (MgO and $CaCO_3$) were studied on the pyrolysis products of waste rubber (Shah et al., 2008). The catalyzed pyrolysis of biomass generally leads to higher yields of water, coke and gases than that of non-catalyzed pyrolysis. However the catalyst application had a significant effect on the bio-oil properties and noticeable improvements in the bio-oil quality.

This spectrum of possible bio-oil production processes stress the need for a comparative analysis that potentially indicates what would be the best approach to use in a biorefinery context. A biorefinery is a conceptual model for future biofuel production where both fuels and high value co-product materials are produced (Fatih Demirbas, 2009). A proper planning of the intended biorefinery scheme must be performed initially. The way the processes are integrated is very important for the desired objectives (Holm-Nielsen and Ehimen, 2014).