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Research paper

## Fractionation of bio-oil produced from hydrothermal liquefaction of microalgae by liquid-liquid extraction

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## ABSTRACT

Fractionation of bio-oil is in favor of upgrading bio-oil to transport fuel or chemicals. The microalgae *Dunaliella tertiolecta* was hydrothermally liquefied to form a bio-oil, which was split into two layers during cooling: the lower layer contained organics with relatively high molar mass from 78 to 389 g mol<sup>-1</sup>, while the super layer with relatively low molar mass from 44 to 121 g mol<sup>-1</sup>. The lower layer of hydrothermally liquefaction (HTL) bio-oil was further fractionated into ethanol phase (oil 1) and dichloromethane phase (oil 2), and the super layer yielded 1 or 3–4 fractions of extracts (oil 3) via single-stage or multistage liquid-liquid extraction respectively. The compositions of each fraction were analyzed by GC-MS in detail. Dichloromethane, chloroform, cyclohexane, benzene, toluene, iso-octanol, petroleum ether, carbon tetrachloride, 1,1,1-trichloroethane, ethyl acetate were compared in terms of their extraction capabilities to organics of bio-oil. The results indicated the chloroform and dichloromethane have the highest comprehensive extraction capabilities. In multistage extraction, when dichloromethane was used as extractant, the extraction distribution ratio (calculated using COD, chemical oxygen demand) was 0.66 in first-stage, then sharply dropped with an increase in stage number, 2nd–3rd stage extractions achieved the maximum extraction percentage (approximately 53%). That the optimum combination of chloroform, benzene and 1,1,1-trichloroethane fractionated the super layer of HTL bio-oil can obtain very low oxygen content fraction: hydrocarbons (purity of hydrocarbons: relative content 97.9%) from the 2nd stage of multistage extraction.

### 1. Introduction

Biomass is a well-known clean and sustainable new energy or chemicals source. As a new energy resource, the available biomass includes sawdust, wood piece, bark, rice husk, straw and stalk of crop, and microalgae. Microalgae has been considered as one of the most promising alternative source for biofuel production due to the fact that it has faster growth rate, higher oil content, and less complex structure than other biomass [1]. Biomasses can be converted to gaseous, liquid (bio-oil) and solid (biochar) fuels through thermochemical treatment including flash, fast, slow pyrolysis or hydrothermal liquefaction (HTL) [2]. By comparison to pyrolysis, the hydrothermal liquefaction process for bio-oil production from microalgae exhibits higher bio-oil yields, lower char yields, and lower energy consumptions [3].

The bio-oil generally contains lower sulfur by contrast with fossil fuels, therefore, it causes negligible or zero emission of SO<sub>2</sub> pollutants when it is used as fuel. But it has several undesired properties such as high oxygen content (containing considerable amount of ketones, phenols, acids, aldehydes, and esters, etc.), high viscosity, high

corrosiveness and low heating value. So, bio-oil must be upgraded before used as a furnace fuel or transportation fuel or valuable chemicals. So far, many methods for upgrading the bio-oil to transportation fuel have been performed, such as solvent (e.g. ethanol) addition [4,5], emulsification [6], esterification [7], hydro-deoxygenation [8–10], catalytic cracking [2], steam reforming [11–13] and extraction of chemicals from bio-oil [14,15], etc. Amongst these methods, however, the solvent extraction to produce high value chemicals is the most promising alternative approach to make use of the bio-oil because of its room temperature operation and low energy consumption resulting in lower cost [2] than that of other upgrading methods.

Garcia-Perez et al. [14] fractionated the bio-oil from vacuum pyrolysis of wood into 6 fractions based on the differences in polarity by solvent extraction using toluene (TOL), methanol, diethyl ether and dichloromethane (DCM) as solvents, and characterized these fractions into 8 chemical families. Kanaujia et al. [15] fractionated the bio-oil obtained from pyrolysis of *Jatropha Curcas* seed cake into several fractions by liquid-liquid extraction (LLE). Karagoz et al. [16] compared the compositions of fractions obtained by solvent extraction of

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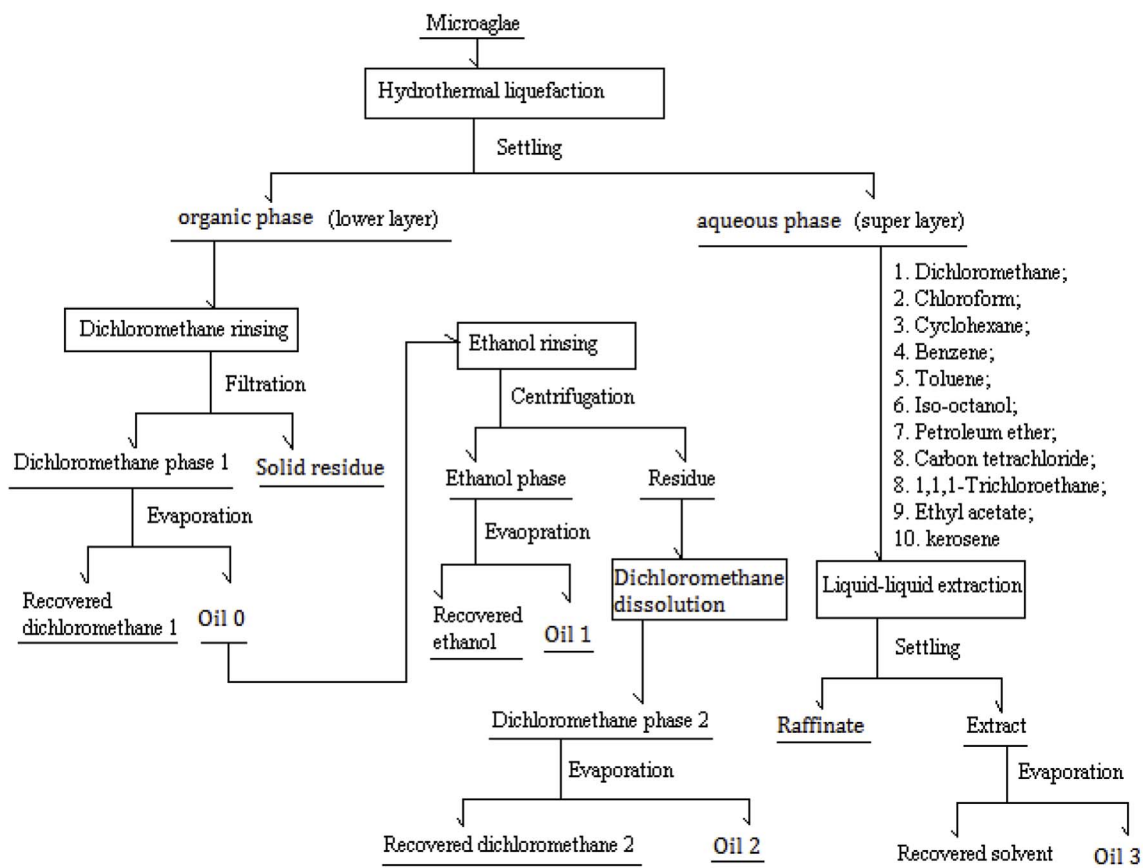


Fig. 1. Fractionation scheme for hydrothermal liquefied bio-oil of microalgae.

bio-oil from hydrothermal liquefaction of sawdust, rice husk, lignin and cellulose, using acetone, diethyl ether and ethyl acetate (EA) as solvents. However, the use of ingenious combination of different solvents to acquire more pure chemicals or single type of compounds, of which the oxygen content is low enough to be directly used as transportation fuels (without further upgrading) via multistage LLE has not been reported so far.

In this paper, the microalgae *Dunaliella tertiolecta* was converted to a bio-oil by HTL, i.e., at a subcritical condition of water, the main components proteins, carbohydrates and lipids of microalgae were decomposed into middle and small molecules to form a bio-oil. Since this bio-oil has similar properties to that of wood-derived bio-oil by pyrolysis, such as high viscosity, high oxygen content except high nitrogen content, the HTL bio-oil could be fractionated into several functional groups by single-stage and multistage LLE. Particularly, we used the combination of several solvents with respective different polarities for separation of organics in a multistage LLE aiming to obtain single type of compounds, such as hydrocarbons. The distribution ratios and extraction efficiencies for single-stage and multistage extraction were determined by analysis of the COD (chemical oxygen demand, which is equivalent to the total concentration of organic compounds in aqueous phase) of the aqueous phase before and after extraction. The compositions of each fraction were investigated by GC-MS in detail, and the bio-oil fractions were characterized in terms of chemical functional groups. This fractionation is in favor of upgrading fractions of bio-oils respectively to excellent transportation fuels or chemicals, or directly obtaining excellent transportation fuel or chemicals without further upgrading. In addition, the use of COD for study of extraction performances is important due to the complexity of chemical composition of bio-oil, and this method has also not been used in investigation of bio-oil in the literatures.

## 2. Materials and methods

### 2.1. Preparation of bio-oil and fractionation strategy

Bio-oil was prepared by HTL of microalgae. The used microalgae, *Dunaliella tertiolecta*, was purchased from Otog banner Rong de algal industry Co., Ltd. (Inner Mongolia, China). This microalgae contains mainly proteins 30.63% (mass), carbohydrates 52.31% (mass) and lipids 5.18% (mass), of which the detail results of compositional and elemental analysis were described elsewhere [17]. In a typical experiment, dried microalgae 18.8 g and water 180 ml were added into the autoclave with capacity 250 ml, stirred at 60 revolutions per minute and heated by an external electrical furnace. When temperature attained 340 °C(14.5 MPa), this temperature was kept constant for 30 min. The accuracy of temperature controlled was  $\pm 0.1$  °C. Then the autoclave was naturally cooled to room temperature and the liquefied product was split into two layers (HTL bio-oil) during cooling. Before opening the autoclave, the gaseous phase product was collected with several 100 ml injectors and analyzed by GC-MS. The super layer of HTL bio-oil, called as aqueous phase, was subjected to LLE; thus obtained extracts were evaporated by a rotary evaporator for removing the corresponding solvents to yield the bio-oil (oil 3). The lower layer, water-insoluble fraction, called as organic phase (tar and solid), was rinsed 2-3 times with totally 100 ml DCM from the autoclave. Thus obtained solid-liquid mixture was filtrated, the solid remaining on the filter paper was washed twice with totally 40 ml DCM and dried at 105 °C for 24 h to form a solid residue, and the filtrate was DCM phase 1, which was evaporated by a rotary evaporator for removal of solvent to produce the bio-oil (oil 0). The oil 0 was dissolved (extracted) with 35 ml ethanol, thus obtained solid-liquid mixture was completely transferred to a centrifugal tube and centrifugally separated into two layers (at 10000 revolutions per minute for 5 min): the super layer,

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