

# UPGRADING OF BIO-OIL IN SUPERCRITICAL CO<sub>2</sub>: EXPERIMENTAL RESEARCH AND LIFE CYCLE ASSESSMENT

Tingyu Wei<sup>1</sup>, Zhongyang Luo<sup>1\*</sup>, Yi Yang<sup>1</sup>, Guoxiang Li<sup>1</sup>, Kongyu Lu<sup>1</sup>, Wenbo Wang<sup>1</sup>, Wenjie Guan<sup>1</sup>  
State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

## ABSTRACT

Research on upgrading of bio-oil in supercritical alcohols shows a potential to produce vehicle fuels from bio-crude. However, the separation of solvent alcohols and upgraded oil remains a problem. In this paper, bio-crude derived from fast pyrolysis of rice husk was upgraded in supercritical CO<sub>2</sub> with the catalysts of Pd, Ru, Pt (supported on activated carbon), in order to recycle the solvent from upgraded oil spontaneously. Results reveal that increase of reaction temperature promotes both esterification reaction and hydrogenation reaction, while increase of initial H<sub>2</sub> pressure promotes the conversion of aldehydes, but decrease the conversion of phenols and sugars. On this basis, the production process of fast pyrolysis and supercritical CO<sub>2</sub> upgrading was established and simulated with Aspen plus software. Through life cycle inventory analysis, the environmental impact of this process were studied, and then compared with upgrading in supercritical ethanol. The result shows weaknesses centered in the agricultural production and upgrading process. At last, the analytic hierarchy process is used to consider the weights of various environmental indicators to obtain a comprehensive LCA result. The final results display a slightly better environmental impact potential than that of ethanol.

**Keywords:** bio-oil upgrading, supercritical CO<sub>2</sub>, life cycle assessment(LCA), the analytic hierarchy process(AHP)

## NONMENCLATURE

### Abbreviations

|     |                             |
|-----|-----------------------------|
| ADP | Abiotic Depletion Potential |
| GWP | Global Warming Potential    |
| AP  | Acidification Potential     |
| HTP | Human Toxicity Potential    |

|                    |  |
|--------------------|--|
| POCP               | Photochemical Ozone Creation Potential                           |
| ODP                | Ozone Depletion Potential  |
| EP                 | Eutrophication Potential   |
| PY-CO <sub>2</sub> | Biomass Pyrolysis and Upgrading in Supercritical CO <sub>2</sub> |
| PY-ETOH            | Biomass Pyrolysis and Upgrading in Supercritical Ethanol         |
| Fin                | Environmental Integrated Index                                   |

## 1. INTRODUCTION

Among different kinds of renewable energy, biomass energy is the only one that can be utilized as carbon source, easily stored and transported, and directly converted into liquid fuel meantime. However, biomass liquefaction technologies are confronted with lots of problems on the way to application, making slower progress than expected. Biomass pyrolysis and upgrading in supercritical alcohols is one of the promising routes of liquid biofuel production, which has been studied widely by many researchers [1], including our group [2-4]. Yet the heavy use of alcohol and the separation between solvent and product really impede further development of industrialization. To get around such problems, it is conceivable to anticipate a substitute solvent that behaves better in desirable physiochemical properties and more friendly in environmental and economic aspects, and supercritical CO<sub>2</sub> is one of the candidates with the advantages of easy accessibility, high separation efficiency, little residue and safety. In this paper, experiments of bio-crude upgrading in supercritical CO<sub>2</sub> were first carried out to find some characteristic and mechanism of the complex reactions, then process simulation and LCA research were conducted to evaluate the feasibility in practical scenarios.

## 2. MATERIALS AND METHODS

### 2.1 Materials and catalysts

Crude bio-oil derived from fast pyrolysis of rice husk was supplied by University of Science and Technology of China. Ru/C, Pd/C and Pt/C purchased from Aladdin were used as catalysts in this work. Ethanol purchased from Sinopharm Chemical Reagent was used as reactant of esterification reaction. CO<sub>2</sub> used as solvent and H<sub>2</sub> were purchased from Jingong Company. All materials were used without pretreatment.

### 2.2 Experimental procedure

All the experiments were carried out in a 500ml stainless steel batch reactor produced by Parr INC. In a standard experiment, 3g Pd/C, 80g crude bio-oil and 40g ethanol were added into the reactor. 5.5MPa CO<sub>2</sub> and 2MPa H<sub>2</sub> were purged into the reactor after flushing the reactor with N<sub>2</sub> for five times. The reactor was heated up to 150 °C in 1 hour and kept for 3 hours. The stirring speed of the agitator was 700rpm during the whole reaction. And after the reaction, the reactor was cooled down to room temperature. Gas products were collected by gas bags and liquid products were collected after separated from catalysts by vacuum filtration. The recovered catalysts were washed by ethanol several times until the filtration was totally colorless.

the carrier gas was nitrogen. The GC-MS operating conditions were as followed: the oven temperature was kept in 40 °C for 3 min, then heated up to 180 °C at 4.0 °C /min, then to 260 °C at 10 °C/min and held at 260 °C for 10 min. Compounds were identified by the National Institute of Standards and Technology (NIST) library. In this paper, the relative content was determined by area normalization. Ethanol was not taken into calculation in this work. The Heating value of the bio-oil was measured by a bomb calorimeter. And water content was measured by a Karl Fisher moisture titrator.

### 2.4 Aspen process modeling and simulation

As shown in Fig.1, the main blocks of the simulation process, both the pyrolysis reactor and the upgrading reactor, were specified as RYield blocks, where the pyrolysis product distribution and related parameters are provided by the research of the University of Science and Technology of China, while the input parameters of upgrading section mainly come from our experimental data, the result of experiment over Ru/C catalyst in particular. Besides, the process of pretreatment of biomass feedstock was briefly simulated and some preliminary waste heat recovery blocks were designed. The energy demanded in this system was mainly met by the combustion (RGibbs) of the by-products.

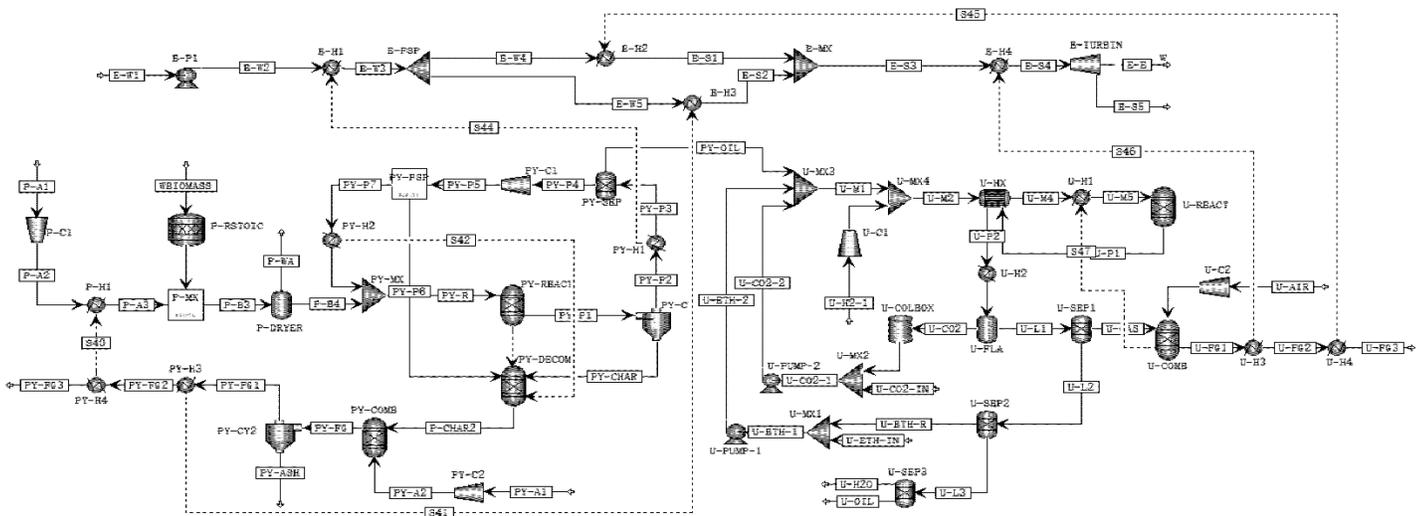


Fig. 1. The flowsheet of upgraded bio-oil production process

### 2.3 Products analysis

The composition of gas products was determined by GC (Agilent 7890A) equipped with both an FID and a TCD detector. Calibrating gas was used to determine H<sub>2</sub> and CO<sub>2</sub>. The chemical composition of liquid product was separated and analyzed by GC-MS with an HP-5column. The injector temperature was 260 °C in split mode and

### 2.5 LCA assumptions and scope definition

LCA was carried out with simplifications and assumptions as follows: 1. the amount of CO<sub>2</sub> that plants fixed is equal to that produced by biomass during production and use, namely carbon neutral apparently, and these offset CO<sub>2</sub> inputs and outputs are omitted in the inventory; 2. environmental impacts of land use and

land use change are not taken into account; 3. factories construction and equipment factors are also ignored in the production process of liquid biofuel.

The data in the agricultural production process mainly comes from the official statistics of the Chinese government [5]. The allocation coefficient is calculated according to economic values, and for the rice husk the number is 0.04. The functional unit is 1MJ upgraded oil.

the commercial software GABI TS is used to calculate the environmental impact potential of the biomass liquefaction route of fast pyrolysis and upgrading in supercritical CO<sub>2</sub>. The system boundary is shown below:

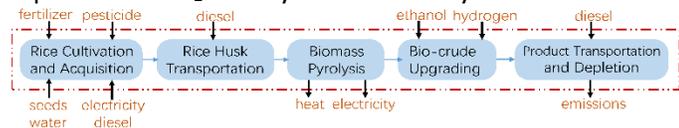


Fig. 2. System boundary of this LCA study

## 2.6 LCA integrated evaluation over AHP

The CML 2001 evaluation method is applied, focusing on the seven indicators of ADP, GWP, AP, HTP, POCP, ODP and EP. On the basis of characterization and standardization, the analytic hierarchy process is used to assign weights to each environmental indicator, and the judgment matrix is as follows. After verification, the random consistency ratio CR<0.1, suggesting the degree of inconsistency is reasonable and acceptable.

Table 1. Relative importance scales of every two sorts of environmental impact indicator

|      | ADP | GWP | AP  | HTP | POCP | ODP | EP |
|------|-----|-----|-----|-----|------|-----|----|
| ADP  | 1   | 2   | 3   | 5   | 5    | 6   | 7  |
| GWP  | 1/2 | 1   | 2   | 5   | 5    | 3   | 4  |
| AP   | 1/3 | 1/2 | 1   | 3   | 3    | 2   | 5  |
| HTP  | 1/5 | 1/5 | 1/3 | 1   | 1    | 2   | 3  |
| POCP | 1/5 | 1/5 | 1/3 | 1   | 1    | 2   | 3  |
| ODP  | 1/6 | 1/3 | 1/2 | 1/2 | 1/2  | 1   | 6  |
| EP   | 1/7 | 1/4 | 1/5 | 1/3 | 1/3  | 1/6 | 1  |

## 3. RESULTS AND DISCUSSION

### 3.1 Experiment results and analysis

#### 3.1.1 Effect of reaction temperature

Water is an important product of esterification. Water content increases with the reaction temperature, which implies a higher reaction temperature promotes the esterification reaction during the upgrading of bio-oil. Among our experiments, 175 °C has the highest content of esters and lowest acids content among these three different reaction temperatures.

H<sub>2</sub> consumption is an important parameter to measure the effect of hydrogenation reaction. With the increase of reaction temperature, the consumption of H<sub>2</sub> increased simultaneously. In 175 °C, 1g crude bio-oil reacts with 65.37ml H<sub>2</sub>, while in 125 °C only 48.34ml H<sub>2</sub> reacts with 1g bio-oil. And the relative content of phenols and aldehydes is lowest in 175 °C while the alcohols content is highest. It can be speculated that phenols and aldehydes reacts with H<sub>2</sub> and produced more alcohols.

#### 3.1.2 Effect of initial H<sub>2</sub> pressure

Initial H<sub>2</sub> pressure mainly effect the hydrogenation reaction. The consumption of H<sub>2</sub> increased rapidly with the increase of initial H<sub>2</sub> pressure. With 1MPa, 2MPa, 3MPa initial H<sub>2</sub> pressure, 1g crude bio-oil reacts with 32.21ml, 51.37ml and 89.03ml. However, H<sub>2</sub> reacts with different reactants in different initial pressure. Fig.3 shows that H<sub>2</sub> reacts with aldehydes and sugars with 2MPa and 3MPa initial H<sub>2</sub> pressure, while it reacts with phenols with 1MPa initial H<sub>2</sub> pressure. Thus 1MPa has the lowest phenols and highest aldehydes and sugars among these three different initial pressure.

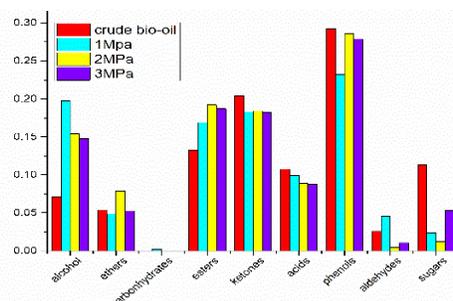


Fig.3. Relative content of bio-oil under different initial H<sub>2</sub>

#### 3.1.3 Effect of catalysts

Catalysts mainly influence the reaction pathways. As shown in Fig.6 Pt/C has the highest amount of sugars, aldehydes and lowest ketones and phenols among three different catalysts. We can speculate that Pt/C has a higher reaction activity with ketones and phenols and lower reaction activity with aldehydes and sugars. Pd/C and Ru/C are quite similar in hydrogenation reactions. In

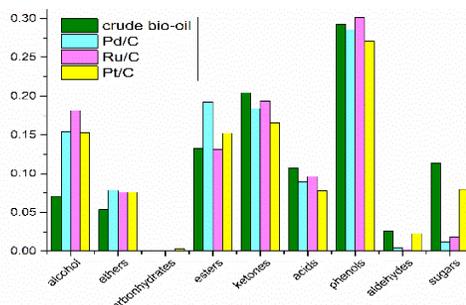


Fig. 4 Relative content of Bio-oil under different catalysts

esterification reaction Pd/C has a higher activity, which results in the highest esters content.

### 3.2 LCA results and analysis

#### 3.2.1 Life cycle impact assessment

The results of process simulation show that the studied production system of supercritical CO<sub>2</sub> upgraded bio-oil can meet the heat duty itself. The balanced mass and energy data is used in the life cycle inventories analysis, as well as some other data from literature and database. Seven selected environment impact category indicators were calculated in Gabi ts, the results after characterization and normalization are summarized in Fig.5. Biomass pyrolysis takes most responsibility for AP because the pyrolysis bio-char and some of the gaseous product are combusted to provide the heat duty of the system, but the flue gas treatment is not in consideration in our simulation. Apart from that, biomass feedstock acquisition and upgrading process are the two centered contributors. EP and OCP may mainly come from the fertilizer and pesticide used in rice growing. Upgrading in supercritical CO<sub>2</sub> still consumes a certain amount of electricity, hydrogen, ethanol, closely related with fossil fuels, resulting in much higher HTP, GWP and ADP.

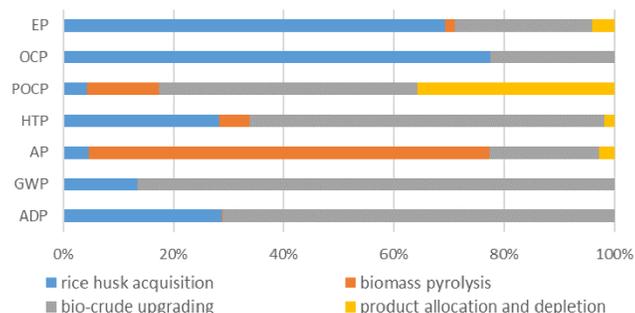


Fig. 5. PY-CO<sub>2</sub> system life cycle environment impact contribution distribution of different stages

#### 3.2.2 integrated LCA indicator over AHP

With the judgement matrix in Table 1, weights of different indicators are calculated and shown in Table 2. Similar simulation and LCIA processes are conducted to the system of PY-ETOH, with experiment data from previous work of our group. LCA results of gasoline acquisition and internal combustion engine use are obtained from literature [6]. Every environment impact potential is normalized by the CML global data updated in Jan. 2016 within Gabi database, and the weighted sum is shown as Fin in Table 2. PY-CO<sub>2</sub> and PY-ETOH show inferior traits on AP and EP, but with the integrated index they both perform better than gasoline. PY-CO<sub>2</sub> is slightly

better choice to the environment on the whole in this case.

Table 2. LCA normalized results and the integrated index over AHP of PY-CO<sub>2</sub>, PY-ETOH and gasoline

| indicator  | weights | PY-CO <sub>2</sub> | PY-ETOH         | gasoline        |
|------------|---------|--------------------|-----------------|-----------------|
| ADP        | 0.363   | 3.74E-13           | 3.57E-13        | 1.23E-09        |
| GWP        | 0.236   | 8.53E-13           | 1.43E-12        | 1.73E-12        |
| AP         | 0.154   | 2.6E-12            | 2.83E-12        | 7.94E-13        |
| HTP        | 0.098   | 6.44E-13           | 9.08E-13        | 3.08E-12        |
| POCP       | 0.060   | 7.72E-13           | 6.85E-13        | 4.76E-13        |
| ODP        | 0.060   | 5.03E-19           | 4.94E-19        | 4.22E-14        |
| EP         | 0.029   | 8.61E-13           | 7.72E-13        | 2.16E-13        |
| <b>Fin</b> | 1.000   | <b>8.72E-13</b>    | <b>1.06E-12</b> | <b>4.46E-10</b> |

## 4. CONCLUSIONS

This paper shows the possibility of ethanol being replaced by CO<sub>2</sub> as the role of supercritical solvent in the process of bio-crude upgrading, at least in environmental priority situation, the substitute is acceptable in rough preliminary consideration, in spite of the fact that this route is still far from non-alcohol, even fossil-fuel-free. And more further work remains to be done when it comes to application in reality.

## ACKNOWLEDGEMENT

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