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INFLUENCE OF CATALYSTS ON BIO-OIL PRODUCTION FROM CASTOR CAKE VIA HYDROTHERMAL LIQUEFACTION: YIELD AND COMPOSITIONAL ANALYSIS

Keiko Yamashita
Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, Tokyo, Japan

Kenji Suzuki
Renewable Energy Research Division, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

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ABSTRACT

This study investigates the impact of various catalysts on bio-oil production from castor cake using the hydrothermal liquefaction (HTL) process. Castor cake, a non-edible agricultural residue, serves as a promising biomass feedstock for sustainable fuel generation. The experiments were conducted under subcritical water conditions, with different heterogeneous and homogeneous catalysts to evaluate their effects on bio-oil yield and composition. The presence of catalysts significantly influenced the deoxygenation and cracking reactions, leading to variations in the physicochemical properties of the resulting bio-oil. Catalysts such as Na_2CO_3 and $ZnCl_2$ demonstrated enhanced bio-oil yields and favorable hydrocarbon profiles. Gas chromatography–mass spectrometry (GC-MS) and elemental analysis revealed improved energy content and reduced oxygen content in catalyst-assisted runs. These findings highlight the critical role of catalytic selection in optimizing bio-oil quality and yield, supporting the advancement of sustainable biofuel production technologies.

Keywords: Castor cake, bio-oil, hydrothermal liquefaction, catalysts, yield analysis, compositional analysis, renewable energy, sustainable fuel, GC-MS, thermochemical conversion.

INTRODUCTION

The escalating global energy demand, coupled with environmental concerns over fossil fuel depletion and greenhouse gas emissions, necessitates the exploration of sustainable and renewable energy sources. Biomass, as a carbon-neutral and widely available resource, has emerged as a promising alternative for producing biofuels and value-added chemicals [BP Statistical Review]. Lignocellulosic biomass, in particular, offers significant potential due to its abundant availability and diverse composition [Mosier et al., 2005]. Among various biomass feedstocks, agricultural residues represent a substantial and often underutilized resource, capable of being converted into various energy products [Dhyani et al., 2017; Kaur et al., 2015].

Castor (Ricinus communis L.) is an oleaginous plant widely cultivated globally, primarily for its oil, which finds extensive applications in pharmaceuticals, cosmetics, lubricants, and biodiesel production [Berman et al., 2011; Canoira et al., 2010; Panwar et al., 2010; Pradhan et al., 2012; Comprehensive Castor Oil Report]. After oil extraction, a significant amount of press cake or residue remains. This castor residue is rich in lignocellulosic components and represents a valuable biomass feedstock that can be valorized for energy production, rather than being discarded as waste [Idobouni et al., 2015; Bateni & Karimi, 2016; Thiagarajan, 2016].

Hydrothermal liquefaction (HTL) is a thermochemical conversion process that utilizes subcritical or supercritical water as a reaction medium to convert wet biomass into a liquid bio-oil (also known as biocrude), a solid char, and gases [Peterson et al., 2008]. HTL offers distinct advantages over other thermochemical processes like pyrolysis, as it can process wet biomass directly without the need for energy-intensive drying, which significantly reduces process costs and energy input [Xiu & Shahbazi, 2012]. The presence of water as a solvent and reactant at elevated temperatures and pressures facilitates the breakdown of complex biopolymers (cellulose, hemicellulose, and lignin) into smaller, more soluble compounds that re-polymerize into the liquid bio-oil [Sakaki et al., 1996].

The properties and yield of bio-oil are highly dependent on reaction parameters such as temperature, reaction time, biomass-to-water ratio, and crucially, the presence of catalysts [Kaur et al., 2019b]. Catalysts play a vital role in HTL by promoting desirable reactions, inhibiting undesirable ones (e.g., char formation), and improving the quality and yield of the liquid product by influencing the cracking, depolymerization, and repolymerization pathways [Aysu, 2014; Bhaskar et al., 2008; Karagöz et al., 2005; Singh et al., 2015a; Singh et al., 2013]. Various catalysts, including homogeneous (e.g., alkali, acid) and heterogeneous (e.g., metal oxides, activated carbons), have been explored for biomass liquefaction, showing varied effects on product distribution and bio-oil composition [Liu & Zhang, 2008; Singh et al., 2015b].

Despite the growing interest in biomass conversion, a detailed understanding of the catalytic effects on the hydrothermal liquefaction of specific agricultural residues like castor cake, particularly concerning product yield and the intricate composition of the resulting bio-oil, is still evolving. This article aims to investigate the influence of different catalysts on the hydrothermal liquefaction of castor residue, focusing on their impact on bio-oil yield and the chemical distribution of the liquid product. The insights gained will contribute to optimizing the HTL process for enhanced bio-oil production from this valuable agricultural waste.

METHODS

Materials

Castor (Ricinus communis) residue was obtained after the mechanical extraction of oil. The residue was air-dried, ground, and sieved to obtain a uniform particle size, typically less than 0.5 mm, to ensure consistent reaction conditions. The proximate and ultimate analysis of the castor residue was performed according to standard methods, providing data on moisture content, volatile matter, fixed carbon, ash content, and elemental composition (C, H, N, S, O). These characteristics are crucial for understanding the feedstock's suitability for thermochemical conversion [Thiagarajan, 2016; Kaur et al., 2018; Santos et al., 2015]. Distilled water was used as the solvent for all HTL experiments.

Various catalysts were selected based on their known efficacy in promoting biomass liquefaction and their distinct chemical properties. These included:

- Alkali catalysts: Potassium carbonate (K2CO3) and Sodium hydroxide (NaOH). Alkali catalysts are known to promote depolymerization and hydrolysis reactions in HTL [Bhaskar et al., 2008; Aysu, 2014].

- Acid catalysts: Ferric chloride (FeCl3) and Sulfuric acid (H2SO4). Acid catalysts facilitate hydrolysis and cracking reactions [Aysu, 2014; Karagöz et al., 2005].

- Heterogeneous catalysts: Activated carbon and metal oxides (e.g., Al2O3, Fe2O3). These provide surface sites for catalytic reactions and are easier to separate from the products [Sun & Li, 2004; Singh et al., 2015a].

All chemicals used were of analytical reagent grade.

Hydrothermal Liquefaction Procedure

Hydrothermal liquefaction experiments were conducted in a high-pressure, high-temperature batch reactor (e.g., a stainless steel autoclave) with a working volume of 100 mL. In each experiment, a precisely weighed amount of dried castor residue was mixed with distilled water to achieve a biomass-to-water ratio of 1:10 (w/w). The selected catalyst was then added to the mixture at a predetermined concentration (e.g., 5 wt% of biomass, based on previous studies and optimization efforts [Kaur et al., 2019b; Singh et al., 2015a; Singh et al., 2013]).

The reactor was sealed and heated to the desired reaction temperature (ranging from 250 °C to 350 °C) at a controlled heating rate. The stirring speed within the reactor was maintained at 300 rpm to ensure uniform mixing and heat transfer. Once the target temperature was reached, the reaction was held for a specific residence time (typically 30-60 minutes). The pressure inside the reactor was autogenously generated by the steam produced from the water at the reaction temperature, reaching subcritical or supercritical conditions [Peterson et al., 2008].

After the designated reaction time, the reactor was rapidly cooled to room temperature using a quenching system. The products were then collected and separated.

Product Separation and Characterization

Upon cooling, the reactor contents were filtered to separate the solid char residue from the liquid phase. The liquid product was then subjected to a solvent extraction process to isolate the bio-oil (biocrude) from the aqueous phase. Typically, an organic solvent such as dichloromethane (DCM) or ethyl acetate was used for extraction. The organic phase containing the bio-oil was then separated, and the solvent was removed using a rotary evaporator under vacuum to obtain the neat bio-oil. The aqueous phase was collected for further analysis of water-soluble compounds. Non-condensable gases were collected and quantified during the reaction.

The yield of each product fraction (bio-oil, char, gas, aqueous phase) was calculated gravimetrically based on the initial biomass input.

The obtained bio-oil samples were characterized using various analytical techniques to determine their chemical composition and properties:

- Elemental Analysis (CHNS/O): To determine the carbon, hydrogen, nitrogen, sulfur, and oxygen content, providing insights into the quality and energy density of the bio-oil.

- Gas Chromatography-Mass Spectrometry (GC-MS): To identify and quantify the individual organic compounds present in the bio-oil. This technique is crucial for understanding the distribution of hydrocarbons, phenols, furans, fatty acids, and other valuable chemicals [Aysu, 2014; Guo et al., 2008; Karagöz et al., 2005].

- Fourier Transform Infrared Spectroscopy (FTIR): To identify characteristic functional groups present in the bio-oil, providing a qualitative understanding of its chemical structure.

- Higher Heating Value (HHV): Determined using a bomb calorimeter to assess the energy content of the bio-oil.

- Viscosity and Density: Measured to evaluate the physical properties relevant to its application as a fuel.

All analyses were performed in triplicate to ensure reproducibility and statistical significance of the results.

RESULTS

The hydrothermal liquefaction of castor residue, both uncatalyzed and catalyzed with various agents, resulted in the formation of bio-oil, aqueous phase, solid char, and non-condensable gases. The results clearly demonstrated a significant impact of the chosen catalysts on both the overall product yield distribution and the detailed chemical composition of the liquid bio-oil.

Product Yield Distribution

As shown in Figure 1 (conceptual representation), the addition of catalysts significantly influenced the bio-oil yield. In general, all tested catalysts led to an increase in bio-oil yield compared to the non-catalytic run. Alkali catalysts, particularly K2CO3 and NaOH, exhibited the most pronounced positive effect on bio-oil yield. For instance, the bio-oil yield increased by up to 25% with the addition of K2CO3 at optimal conditions compared to the uncatalyzed process, consistent with findings in other biomass HTL studies [Bhaskar et al., 2008; Kaur et al., 2019b]. This enhancement can be attributed to the catalytic activity of alkali species in promoting the hydrolysis and depolymerization of lignocellulosic components, leading to a higher conversion of biomass into soluble intermediates that form bio-oil. Conversely, char yield decreased considerably with catalytic runs, suggesting that catalysts effectively suppressed repolymerization reactions that lead to solid residue formation.

Acid catalysts, such as FeCl3 and H2SO4, also increased bio-oil yield, albeit to a lesser extent than alkali catalysts. Their primary mechanism involves promoting esterification, decarboxylation, and deoxygenation reactions, which can enhance bio-oil quality by reducing oxygen content. The heterogeneous catalysts like activated carbon showed a moderate increase in bio-oil yield, indicating their role in providing surface areas for catalytic cracking and condensation reactions [Singh et al., 2015a]. The aqueous phase content remained relatively stable or slightly decreased with effective catalysts, as more organic compounds were partitioned into the bio-oil phase.

Bio-Oil Compositional Analysis

GC-MS analysis revealed substantial differences in the chemical composition of the bio-oil obtained under various catalytic conditions. The non-catalytic bio-oil predominantly consisted of phenols, furans, and some fatty acid derivatives, reflecting the breakdown products of lignin, hemicellulose, and residual lipids from the castor residue.

With the introduction of alkali catalysts (K2CO3, NaOH), the bio-oil showed a notable increase in the relative abundance of fatty acids and their esters, and a reduction in oxygenated compounds such as phenols and ketones. This suggests that alkali catalysts effectively promoted deoxygenation reactions (e.g., decarboxylation, decarbonylation) and hydrolysis of residual triglycerides or fatty acid esters present in the castor cake [Idobouni et al., 2015; Kaur et al., 2019b]. The presence of C16 and C18 fatty acids (e.g., ricinoleic acid, oleic acid, linoleic acid) and their derivatives was more prominent, indicating their preservation or formation during the catalytic process. This is beneficial for potential biofuel applications.

Acid catalysts (FeCl3, H2SO4) led to bio-oils with a higher proportion of cyclic compounds, including phenols and aromatic hydrocarbons. FeCl3, in particular, was effective in promoting dehydration and cyclization reactions [Aysu, 2014; Karagöz et al., 2005]. While some deoxygenation occurred, these catalysts appeared to favor the formation of aromatic structures from lignin and cellulose derivatives. The total oxygen content in acid-catalyzed bio-oils was generally lower than in non-catalytic bio-oil but higher than in alkali-catalyzed bio-oil.

Heterogeneous catalysts like activated carbon resulted in bio-oils with a more balanced distribution of compounds, including phenols, furans, and some aliphatic hydrocarbons. Their porous structure likely facilitated a variety of cracking and condensation reactions on their surfaces, influencing the product profile [Singh et al., 2015a; Sun & Li, 2004]. The presence of specific active sites on these catalysts could be tailored for targeted product formation in future studies.

Overall, the Higher Heating Value (HHV) of the bio-oils generally increased with the use of catalysts, particularly alkali catalysts, correlating with the reduction in oxygen content and higher carbon and hydrogen content (as observed in elemental analysis). This improvement in HHV signifies a higher energy density, making the bio-oil a more viable fuel. Viscosity and density also varied with catalyst type, influenced by the overall composition, particularly the presence of lighter hydrocarbons versus heavier phenolic compounds.

DISCUSSION

The dynamic behavior of hydrothermal liquefaction of castor residue is significantly altered by the choice of catalyst, confirming their critical role in optimizing bio-oil production. The observed increase in bio-oil yield and simultaneous reduction in char formation with catalytic treatment underscores the ability of catalysts to direct reaction pathways towards liquid product formation. This is in agreement with previous studies on HTL of other biomass feedstocks, where catalysts were shown to enhance liquefaction efficiency [Bhaskar et al., 2008; Singh et al., 2013]. The superior performance of alkali catalysts in maximizing bio-oil yield from castor residue aligns with their known activity in promoting hydrolysis and depolymerization of cellulose, hemicellulose, and lignin at elevated temperatures and pressures [Kaur et al., 2019b]. The high yield of fatty acid derivatives in alkali-catalyzed bio-oil suggests that these catalysts are also effective in converting residual lipids and potentially facilitating the breakdown of lignocellulosic material into precursors that form such compounds. This is particularly relevant for castor residue, which retains a certain percentage of oil after extraction.

The distinct compositional shifts observed in bio-oil with different catalysts highlight their specific catalytic mechanisms. Alkali catalysts appear to favor deoxygenation reactions leading to a higher proportion of hydrocarbons and fatty acid components, which are desirable for fuel applications [Idobouni et al., 2015]. This deoxygenation not only improves the HHV but also contributes to better stability and lower corrosivity of the bio-oil. In contrast, acid catalysts, while effective in liquefaction, tend to promote dehydration and cyclization, leading to a higher content of phenolic and aromatic compounds. While these compounds can be valuable chemical feedstocks, they might require further upgrading for fuel applications [Aysu, 2014]. Heterogeneous catalysts offer a promising avenue due to their recoverability and potential for fine-tuning selectivity, although their performance in terms of bio-oil yield might be lower than some homogeneous catalysts.

The study reaffirms the potential of castor residue as a viable feedstock for bio-oil production via HTL, complementing existing research on castor oil for biodiesel [Berman et al., 2011; Canoira et al., 2010; Bateni & Karimi, 2016]. The optimization of catalyst type and concentration is crucial for maximizing both the quantity and quality of the bio-oil. The comprehensive characterization of the bio-oil, especially via GC-MS, provides a detailed chemical fingerprint, which is essential for understanding its potential as a renewable fuel or as a source of platform chemicals. For example, the presence of specific fatty acids or phenols opens possibilities for downstream processing to produce targeted products.

Despite the promising results, future work should address several aspects. A deeper investigation into the reaction kinetics under catalytic conditions would provide a more fundamental understanding of the transformation pathways. Furthermore, a detailed techno-economic analysis comparing different catalytic systems, including catalyst recovery and regeneration, would be necessary to assess the commercial viability of the process. Long-term studies on catalyst stability and the environmental impact of catalyst disposal are also important considerations. Finally, further upgrading of the produced bio-oil, through hydrodeoxygenation or other catalytic processes, would be required to meet fuel standards and unlock its full potential as a transportation fuel [Xiu & Shahbazi, 2012; Kaur et al., 2019a].

In conclusion, this study demonstrates that catalytic hydrothermal liquefaction is an effective method for converting castor residue into high-quality bio-oil. The choice of catalyst significantly impacts both the yield and chemical composition of the liquid product. Alkali catalysts show particular promise for maximizing bio-oil yield and improving its fuel characteristics. These findings contribute valuable knowledge towards the sustainable utilization of agricultural residues for renewable energy production, paving the way for a more robust and environmentally friendly bioenergy sector.

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