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Catalytic Upgrading of Bio-oil from *Ulva lactuca* using Amberlyst-15 Catalyst: Experimental and Kinetic Model

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ABSTRACT

Catalytic pyrolysis of *Ulva lactuca* macroalgae was studied over Amberlyst-15 catalyst at temperature 400, 500, and 600 °C. The comparison between catalytic and non-catalytic pyrolysis in the conversion of *Ulva lactuca* was determined. Intriguingly, it was found that Amberlyst-15 catalyst improved bio-oil production efficiency. The highest bio-oil yield of 29.54 wt% was achieved at 600 °C with the presence of an Amberlyst-15 catalyst. Furthermore, Amberlyst-15 catalyst could enhance gas production by over 73.88%. It could be attributed due to the catalytic pyrolysis could promote more small molecules that are more volatile through a cracking process. Elemental and functional groups in pyrolytic bio-oils were identified via GC-MS analysis. The acidity and structure of Amberlyst-15 catalyst significantly affected the distribution of product components, especially the formation of aromatic hydrocarbons, with a 27.78% relative yield. The first-order kinetic model showed that the production of aromatic hydrocarbons follows Arrhenius law.

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Graphical Abstract
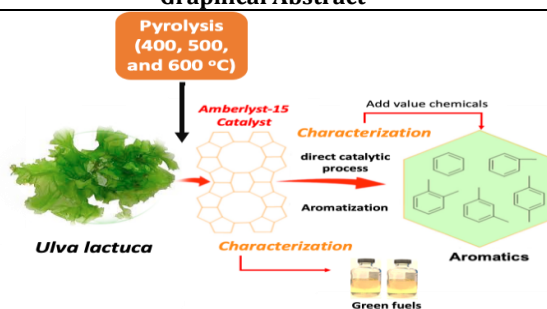
1. INTRODUCTION

Due to its widespread availability and capacity to be farmed on a massive scale, biomass has become an attractive option for renewable energy use in recent years [1, 2]. Rising oil prices and concerns about the impact of human activity on the environment drive these trends.

Biomass is a readily available and cost-effective energy source that may be used for various purposes, including generating heat and electricity, manufacturing chemicals, and providing fuel for transportation [3]. Therefore, researchers are looking for different energy sources, such as substituting biomass with lignocellulosic materials, agricultural wastes, and aquatic environment waste. In

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recent years, macroalgae and aquatic macrophytes have received a lot of attention since their production rate is more significant than that of agricultural and forest biomass [1, 4]. In addition, the limited data on the pyrolysis of aquatic biomass [5, 6] demonstrated that algal bio-oil is greater than lignocellulosic bio-oil in several aspects.

The thermochemical and biochemical/biological processing technologies are the two basic techniques by which biomass obtained from various resources can be converted into a form of energy that can be utilized. The thermochemical process can undergo several stages, including pyrolysis/gasification, liquefaction, and combustion [7-9]. However, digestion and fermentation are both viable options for biochemical conversion [10]. Thermochemical conversion of biomass via pyrolysis provides an alternative route to fuel production [3, 11]. Pyrolysis is the thermally decomposition of organic compounds into several phases of an energy-rich product in an atmosphere free of oxygen. The pyrolysis process generates several different final products, including liquids (bio-oil) and solids (bio-char), and gases (syngas) [12]. In this context, the term "bio-oil" refers to the liquid byproduct of pyrolysis. It is a complex mixture of hydrocarbons and water. There is potential for this oil to be used as a chemical feedstock and an alternative to transportation fuel [13, 14]. However, from several pyrolysis studies for bio-oil production, such as purun tikus [15], empty fruit bunch (EFB) [16], and Crofton weed [17], the characteristics of bio-oils obtained contain high acetic acids, which directly cannot be used. Therefore, there is an urgent need to improve the quality of bio-oil obtained from pyrolysis.

To address this issue and improve the quality of bio-oil, in-situ catalytic pyrolysis is the term employed to describe improving the quality of the bio-oil product directly within the reactor. This process involves the use of catalysts and a biomass mixer. Several researchers investigated catalytic pyrolysis using zeolite, and they noticed that the bio-oil produced undergoes deoxygenation and produces aromatic hydrocarbons and nitrogen-containing molecules [18, 19]. Thangalazhy-Gopakumar et al. [20] examined the catalytic pyrolysis of *Chlorella vulgaris* biomass with HZSM-5 and found that the aromatic hydrocarbon increased from 0.9% to 25.8%. Hematkhah et al. [21] investigated the direct pyrolysis of the microalgae *Spirulina* sp. with the zeolite-based catalysts at 425-625 °C. The introduction of the catalyst increased both the high heat value and the bio-oil energy yield. Thus, the use of zeolite-based catalysts during co-pyrolysis may be a new route for high-value-added compound production. It also increases the aromatic oil by causing deoxygenation, decarboxylation, and dehydration [22].

Anand et al., [23] used several catalysts (ZYH, ZYNa, MgO, ZrO$_2$, and TiO$_2$) to catalytically pyrolyze *Shizochytrium limacinum* biomass at 350–800 °C. At 400 °C, ZYH60, TiO$_2$, and ZYH30 catalysts enhanced nitrogen-containing compounds by 12.22, 12.75, and 19.32 area%. They saw that the catalyst enhanced the amide dehydration process, producing nitriles. Wang et al. [24] observed similar results while studying *Enteromorpha* growth. Bio-oil had 13.77–36.2% nitrogen compounds. Mg-Ce/ZSM-5 catalysts produced the most nitrogen-containing compounds, while ZSM-5 catalysts produced less. Catalytic pyrolysis of *Chlorella vulgaris* was studied by Zainan et al. [25] using a range of Ni-supported zeolites catalyst concentrations. More hydrocarbons and fewer oxygenated and acidic compounds were generated during catalytic pyrolysis than non-catalytic pyrolysis. Catalyst processing did not alter bio-oil yield. However, it had an impact on the composition. According to Uslamin et al. [26], loading Ga onto ZSM-5 changes the acidic characteristics by adding Lewis acid sites and replacing Bronsted acid sites, enhancing aromatic compound selectivity. Therefore, proper acid sites are crucial in developing catalysts since they affect the system's selectivity and coke generation [27].

Previous studies give insights that acid catalyst could enhance the hydrocarbon and suppress the oxygenated compounds. However, bio-oil production from *U. lactuca* with the presence of Amberlyst-15 has not been studied well. Therefore, this study aims to investigate the effect of temperature and catalyst on product distribution and kinetic model in detail. The novelty of this finding highlights the use of Amberlyst-15 catalyst to enhance the high aromatic yields that can improve bio-oil quality. A systematic analysis of bio-oil and bio-char products was also evaluated to determine their physicochemical properties.

2. MATERIALS AND METHODS

2. 1. Preparation of Raw Materials　　*Ulva lactuca* feedstock was collected from Ekas Beach (Lombok Island, West of Nusa Tenggara, Indonesia). Deionized water and ordinary tap water were used to remove sand and other contaminants from the sample. After washing, samples were dried overnight at 105 °C in an oven. The macroalgae were dried, then pulverized into a powder, and sieved at 0.25 mm. Amberlyst-15 catalysts were purchased from Merck KGaA (Darmstadt, Germany) with a particle size of 0.355-1.18 mm, a concentration of H$_2$ ion concentration of 4.7 meq./g dry, surface area 50 m^2/g, porosity 0.36 ml pore/mL bead, pore diameter 240 A°.

2. 2. Reaction procedure　　A 20 g of feedstock was fed into the reactor (350 mm height, 38 mm inner diameter). The experimental set up is shown in Figure 1.
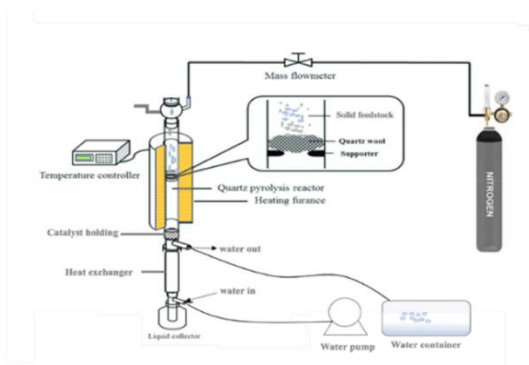
Figure 1. Experimental apparatus

Before each experiment, 2 wt% of the catalyst was suspended from the reactor's top in a quartz hopper. After evaluating the device for gas tightness, 30 mL/min of continuous N_2 was utilized to remove excess air. Subsequently, the reactor's temperature was increased from its initial setting of 25°C to the desired temperatures of 400, 500, and 600°C. Prior studies support this condition. After heating to appropriate temperatures, the reactor was maintained for 1 h. A thermocouple measured the reactor's temperature. The measuring cylinder contained condensable volatiles. The atmosphere was purged of non-condensable gas. By using ether solvent, the organic and aqueous fractions were separated. The reactor was cooled after each analysis. Every preliminary step had to be repeated to determine the quantity of bio-oil produced and get the correct data. The amount of biochar produced was determined by comparing the initial and final masses of the quartz reactor. The percentage of gas produced (in terms of weight) was calculated as the mass difference between the bio-oil and bio-char yields. The following formulas are used to determine product yield [8].

$$\text{Bio-oil yield (wt\%)} = \frac{(W_2)-(W_1)}{Weight\ of\ feedstock} \ x\ 100 \qquad (1)$$

$$\text{Bio-char yield (wt\%)} = \frac{(W_4)-(W_3)}{Intial\ mass\ of\ feedstock\ (g)} x\ 100 \qquad (2)$$

$$\text{Gas yield (wt\%)} = 100\% - (bio - oil\ yield\ (wt\%) + bio - char\ yield\ (wt\%)) \qquad (3)$$

where w_1 is empty measuring cylinder weight, w_2 is measuring cylinder weight with bio-oil, w_3 is empty reactor weight, and w_4 is reactor weight after reaction.

2. 3. Feedstock and Products   Analysis for the study on thermal degradation, a Shimadzu DTG-60 was used for thermogravimetric analysis (TGA). For this study, 5-7 mg of biomass was heated from 25 - 900 °C at a rate of 10 °C per minute in an N_2 atmosphere. FT-IR was performed using a NEXUS670, and the sample

powder was immersed in KBr before analysis. The spectral band that was utilized was 4000 to 400 cm^{-1}. Scans have been captured at a resolution of 4 cm^{-1}. A new baseline was established for the original data, and the adjusted data was then normalized. Bio-oil was investigated using gas chromatography and mass spectrometry (GC/MS-QP2010 SE–Shimadzu, Japan) with an Rtx®-5MS capillary column. Before introducing the bio-oil to the GC/MS, it was diluted with dichloromethane in a 1:4 volume ratio (v/v). The oven was heated to 40 ºC for one minute. After that, the temperature was raised to 10°C per minute for several minutes untill it reached to 150 ° C. The temperature rose at a rate of 10 °C per minute until it reached 300°C, where it remained stable for 30 minutes. Lastly, the device was kept at a temperature of 250 °C. The GC/MS was filled with up to 1 L of the bio-oil that had been dissolved. The compounds that comprise bio-oil have been identified using the mass spectra in the NIST2008 c2.0/Xcalibur data set. The ultimate analysis was performed with the assistance of a CHNS/O analyzer, and the findings were previously reported [8].

3. RESULTS AND DISCUSSION

3. 1. TGA Analysis of the Feedstock and Catalyst Initially, the thermal degradation properties of the original feedstock and Amberlyst-15 were investigated to identify the structural stability and produced types, which is essential for a reasonable elucidation of Amberlyst-15's practical function during the pyrolysis process. The TG and DTG curves of the raw material are displayed in Figure 2(a).

There are three primary steps in the pyrolysis of raw materials. Internal moisture was driven out in the first phase (between 100 and 260 °C), and low molecular weight components were volatilized as indicated by Chen et al. [28] and Dewangan et al. [29]. It was formerly argued that temperatures from 268 to 498 °C were essential for the decarboxylation, depolymerization, and cleavage of carbohydrates, lipids, and proteins during stage 2 of the reaction [30]. This trend was also in line with previous research reported by White et al. [31 and D'Almeida et al. [32], who mentioned that the temperature range of 300–500 ºC was responsible for the decomposition process of lipids and proteins. The third stage of biochar pyrolysis occurred at temperatures between 415 and 657 °C, and it was characterized by a steady, soft weight loss [33]. The TG and DTG curves of the Amberyst-15 catalyst are illustrated in Figure 2(b).

The temperature profile at which catalyst degradation began could potentially be calculated with the use of this interpretation. The heating process typically consists of three distinct phases of degradation. The process started at room temperature and increased to 110 ºC when water

(a)

(b)
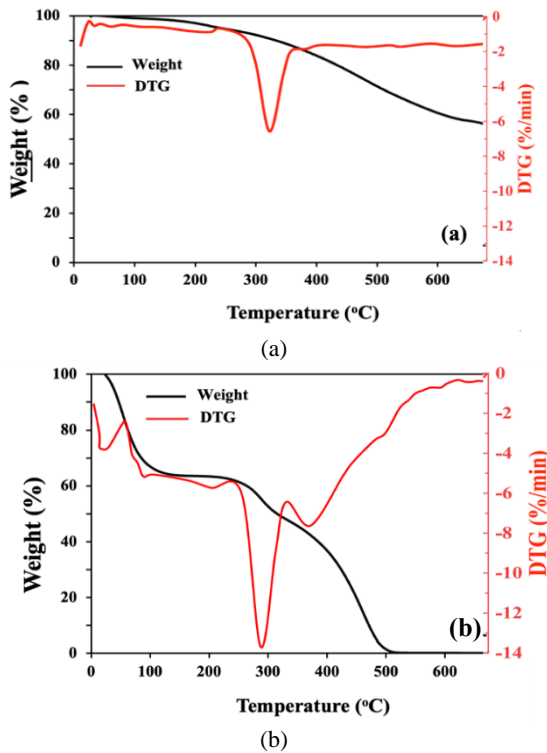
Figure 2. (a) The TG and DTG curves of raw material, (b) The TG and DTG curves of the catalyst

was evaporated. The subsequent stage, between 280 and 480 °C, had the most significant weight loss, and the third stage, between 500 and 700 °C, showed the least weight loss.

3. 2. Product Yield Distribution
3. 2. 1. Effect of Temperature
The effects of temperature (400, 500, and 600 °C) on the pyrolysis of macroalgae (*Ulva lactuca*) were investigated in the presence of nitrogen for 60 min. Figure 3 illustrates the observed percentage of product yield that was achieved.
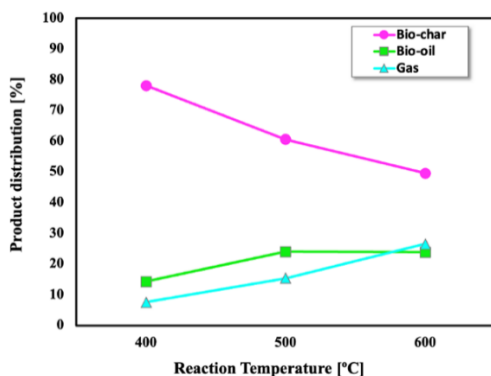
At a pyrolysis temperature of 400°C, the bio-oil produced was 14.32 wt%. Increasing the reaction temperature from 400 to 500 °C increased bio-oil production. However, it dropped during the reaction from 500 °C to 600 °C. The highest bio-oil production (24.05 wt%) was achieved at 500 °C. However, as the temperature was increased to 600 °C, the bio-oil production dropped to 23.87 %. Therefore, 500 °C was optimal for the pyrolysis of *Ulva lactuca* algae, resulting in the complete breakdown of all algae links and a high liquid yield. Several research teams noticed an increase in char production after observing a rise in the re-polymerization of the decomposition intermediates [3, 34, 35]. At temperatures above 400°C, some short-chain liquid products are converted into non-condensable gases, increasing the yield of gases. These results follow the former research of Yorgun et al. [36], who reported that higher temperatures, longer reaction times, and lower heating rates lead to greater yields of gaseous products. Furthermore, biochar yield decreased with increasing temperature, possibly due to a secondary reaction occurring at elevated temperatures [37].

3. 2. 2. Effect of Catalyst Addition
Catalysts (Amberlyts-15) can be used to significantly modify the product yield from the pyrolysis of algal biomass. The yield production comparison of catalytic and non-catalytic pyrolysis yields is shown in Figure 4.

It was found that employing the Amberlyst-15 catalyst throughout the pyrolysis increased the amount of bio-oil produced, which reached 24.9 wt% to 29.54 wt%. In terms of gaseous production, Amberlyst-15 produced 21.57 wt% of gas. This percentage continued to increase as the reaction temperature increased to 600 °C, because greater temperatures caused algae to break down quickly [38]. In contrast, the biochar yield was decreased by employing the Amberlyst-15 catalyst. A similar situation was found in the experimental results of catalytic pyrolysis by Tan et al. [39]. So, the acidity-basicity, pore size, and surface area of catalysts make it possible to turn

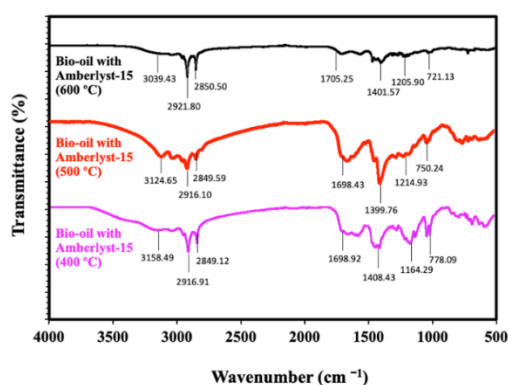**Figure 3.** Effect of pyrolysis temperature on products yield distribution
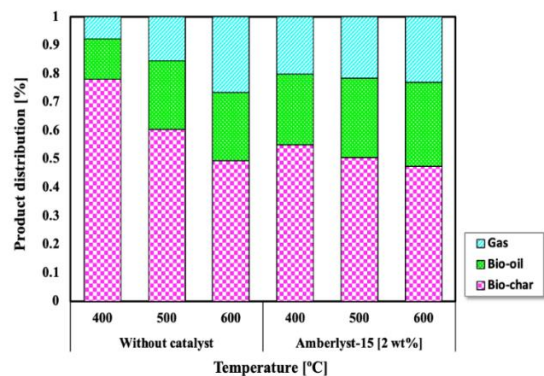
Figure 4. Effect of catalyst addition on products yield distribution

most biomass into products [40]. Mo et al. [37] applied catalytic pyrolysis of macroalgae and obtained 43.6 % bio-oil at 400 °C, which was higher than this study. This may be due to adjustments in the reactor types that were employed.

3. 3. Characterization of bio-oil
3. 3. 1. FT-IR of Bio-oils
Bio-oil has been analyzed using FT-IR to determine the presence of the various functional groups, as indicated by its different fundamental vibrational bands (Figure 5).

The presence of a –OH functional group was determined by observing a band at 3039 – 3158 cm^{-1}. These results, along with the previous result by Pato et al. [41] and Asadpour et al. [42], found that the dominant peak was at 3419.03 cm^{-1}, referring to the stretching vibrations of the –OH group. The asymmetric and symmetric –CH vibrations corresponded to two different vibrational bands at 2916 and 2850 cm^{-1}, respectively. The high hydrocarbon concentration in the bio-oil obtained at 600 °C allowed for observing the band with a high intensity of -CH. In the meantime, the basic vibration of ketone was detected in all of the bio-oils between 1698 and 1700 cm^{-1}. This bright band was detected in non-catalytic bio-oil containing more acid and ester molecules. A lower band at 1698 cm^{-1} was identified, which was attributed to the amide's conjugated carbonyl group, as reported by Biswas et al. [43]. Furthermore, the C = C vibration of alkenes, generated during the pyrolysis of macroalgae, was shown as the fundamental vibration at 1399–1408 cm^{-1}. At 1164–1214 cm^{-1}, the primary groups of aromatic compounds were found to be stretching; this showed that bio-oil was composed of aromatic compounds. Several groups associated with out-of-plane C-H bending have been found in the band region from 700 to 800 cm^{-1}. All bio-oils had similar peak patterns in their spectra; only the strength of the functional bands varied. The fundamental vibration of ketones and acids showed the lipid content

of macroalgae that changed into ester or amide compounds.

3. 3. 2. GC/MS Analysis of Bio-oil
To identify the components found in bio-oils, a GC–MS analysis was carried out. It was shown that bio-oils used in catalytic reactions had a different chemical composition than those used in non-catalytic reactions. The percentages of peak areas for each type of chemical are shown in Figure 6(a). Based on their functional groups, the compositions of pyrolysis volatiles, such as phenols, furans, alkanes, and ketones, as well as acids, alcohols, aromatic hydrocarbons, and N-containing mixtures, were determined.

It can be observed that most of the *Ulva lactuca* pyrolysis bio-oil contains acids (50.3–58.5%), ketones (0.65– 3.5%), N-containing mixtures (3.1–18.8%), aromatic hydrocarbons (3.7–12.4%), phenol (2.9–9.7%) followed by a temperature of 400–600 °C respectively, as well as several other chemical compositions which are only found at a temperature of 400 °C such as alcohol (4.5%), alkanes (9.2%) and small amounts of furan. Introducing a catalyst to the pyrolysis reaction resulted in a significant change in the bio-oil's chemical composition. Catalytic pyrolysis (*Ulva lactuca*-Amberlyst-15 at 400–600 °C) bio-oil majorly contains acid (42.8–53.5%), ketones (2.3–9.7%), N-containing mixtures (1.3–1.5%), aromatic hydrocarbons (11.5–

Figure 5. Fourier transform-infra red spectroscopy (FT-IR) of bio-oils

(a)

(b)
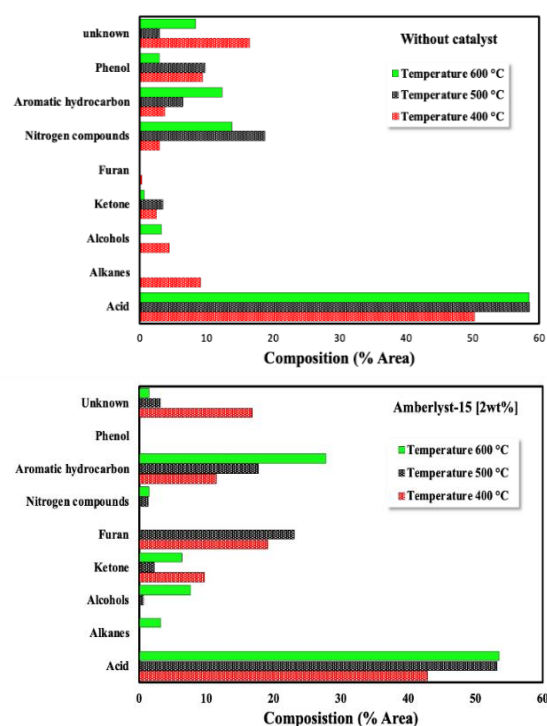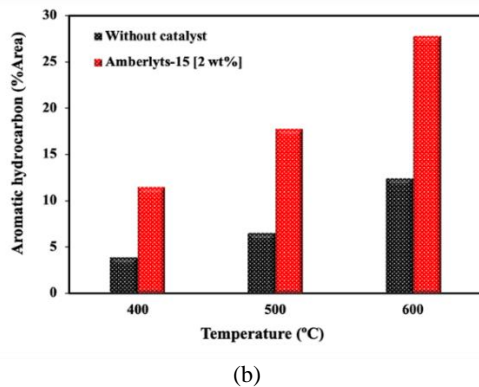
Figure 6. (a) GC/MS analysis of bio-oil (non-catalytic and catalytic pyrolysis), (b) The aromatics hydrocarbon produced from *Ulva lactuca* with and without catalyst

27.8%), at temperature 400–600 °C, respectively. This finding was also in line with a previous study by Xia et al. [44], who observed that at high temperatures, the polymerization and dehydrogenation of oxygen-containing organics probably led to aromatics formation. On the other hand, several chemical compositions were not detected at all reaction temperatures, including furan (19.1–23.1%), which was only detected at 400 and 500 °C, alcohol (0.6–7.6%) at 500 and 600 °C, and approximately 1.5–16% chemical composition that was not detected in pyrolysis integrated with the catalyst. Figure 6(a) shows that phenols, nitrogen-containing chemicals, furans, aromatic compounds, and acids dominate the pyrolysis bio-oil derived from the original macroalgae sample. However, due to the high oxygen concentration and corrosive, the acids can quickly degrade bio-oil, decreasing its quality. In addition, bio-oil can be challenging to utilize due to its high nitrogen concentration and complicated chemical composition. Therefore, it is essential to transform the bio-oils composition towards aromatic hydrocarbons and lower the concentration of acids and nitrogen-containing compounds. Amberlyst-15 and other catalysts substantially promoted the number of aromatic compounds while substantially reducing the formation of acids, phenols, and furans.

Figure 6(b) shows the aromatics hydrocarbon produced from *Ulva lactuca* without and with the Ambelyts-15 catalyst.

It can be pointed out that the aromatic hydrocarbon content in the bio-oil produced by catalytic pyrolysis of macroalgae increased as temperature, reaching a higher level than the original feedstock at temperatures ranging from 400 to 600 °C (11.5–27.8% area). Decarboxylation reactions contributed to hydrocarbon formation during catalytic pyrolysis [45].

3. 4. Rate of Aromatic Hydrocarbon Production
The kinetics of aromatic hydrocarbon production during pyrolysis were examined to quantify the aforementioned temperature impacts. Assuming that the conversion process follows the first-order Arrhenius rate law in terms of the amount of aromatic hydrocarbons, the following equation can be obtained:

$$\frac{d_{ah_x}}{dt} = k_0 \left\{ \exp\left(\frac{-E_a}{RT}\right) \right\} (ah_0 - ah_x) \tag{4}$$

which leads to

$$ah_0 - ah_x = ah_0 exp\left[-k_0 \left\{\exp\left(\frac{-E_a}{RT}\right)\right\}t\right] \tag{5}$$

$$ah_{production} = \frac{ah_x}{ah_0} = 1 - exp\left[-k_0 \left\{exp\left(\frac{-E_a}{RT}\right)\right\}t\right] \tag{6}$$

where ah_0 is the initial amount of aromatic hydrocarbon [%], ah_x is the amount of aromatic hydrocarbon of pyrolyzed bio-oil [%], k_0 is a pre-exponential factor [s^{-1}], E_a is activation energy [J/mol], R is the gas constant [J mol^{-1} K^{-1}], t is time [min], T is temperature [K].

The parameters in Equation (3) have been determined by fitting the experimental data of aromatic hydrocarbon production shown in Figure 7.

The production rates of aromatic hydrocarbons could be well explained by using an Arrhenius equation of the first order. By addressing kinetic parameters, activation energy (E_a) refers to the energy needed to break a bond for a reaction to occur. In contrast, the pre-exponential factor (A) denotes the rate at which the reaction takes place [46]. Catalytic pyrolysis (*Ulva lactuca*-Amberlyst-15) had an activation energy (E_a) of 15.3 kJmol^{-1} and pre-exponential factor (A) of 35.1 min^{-1} which was lower than that for the original pyrolysis feedstock (43.31 kJmol^{-1}, 47.5 min^{-1}) respectively. It shows that using Amberlyst-15 lowers the energy barrier of the pyrolysis process. This means that even though Amberlyst-15 may lower the energy barrier, pyrolysis steam in the pores of the catalyst goes more slowly. This is another reason solid material gets lower slowly when Amberlyts-15 is used because the reaction rate is slow; a second reaction occurred on the catalyst's surface, which led to coking [47].
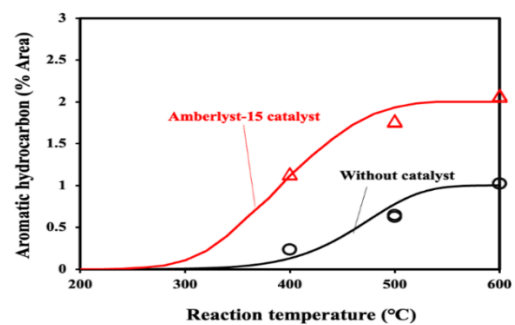
Figure 7. The aromatic hydrocarbon production from the experiment (symbol) and kinetic model (line) for both catalytic and non-catalytic pyrolysis

4. CONCLUSION

One possible thermochemical strategy for improving bio-oil yields and quality is the catalytic pyrolysis of *Ulva lactuca* aquatic biomass. At a maximum temperature of 600 °C, the Amberlyst-15 catalyst produced the greatest amount of bio-oil (29.54 wt%), in contrast to the non-catalytic pyrolysis yield (23.87 wt%). The composition of the pyrolysis liquid yield is improved by exchanging radicals, cracking, or compound ordering during catalytic pyrolysis. The acidity and framework of Amberlyst-15 significantly affected the distribution of product components, particularly aromatic hydrocarbon yield. In generating aromatic hydrocarbons in the upgraded bio-oils, the Amberlyts-15 catalyst was the most active, resulting in the greatest relative percentage of 27.78%. Finally, the production of aromatic hydrocarbons was modeled with first-order kinetics and an Arrhenius equation rate constant, and the reaction parameters were determined for both catalytic and non-catalytic pyrolysis.

5. ACKNOWLEDGEMENT

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Persian Abstract

چکیده

تجزیه در اثر حرارت کاتالیزوری ماکروجلبک Ulva lactuca بر روی کاتالیزور Amberlyst-15 در دمای ۴۰۰، ۵۰۰ و ۶۰۰ درجه سانتیگراد مورد مطالعه قرار گرفت. مقایسه بین تجزیه در اثر حرارت کاتالیزوری و غیر کاتالیستی در تبدیل Ulva lactuca تعیین شد. به طرز جالبی مشخص شد که کاتالیزور Amberlyst-15 راندمان تولید روغن زیستی را بهبود می بخشد. بالاترین بازده روغن زیستی با ۲۹.۵۴ درصد وزنی در دمای ۶۰۰ درجه سانتی گراد با حضور کاتالیزور Amberlyst-15 بدست آمد. علاوه بر این، کاتالیزور Amberlyst-15 می تواند تولید گاز را تا بیش از ۷۳.۸۸ درصد افزایش دهد. این را می توان به این دلیل نسبت داد که تجزیه در اثر حرارت کاتالیزوری می تواند مولکول های کوچک بیشتری را از طریق فرآیند ترک خوردگی فرار هستند، ترویج کند. گروه‌های عنصری و عاملی در روغن‌های زیستی پیرولیتیک از طریق آنالیز GC- MS شناسایی شدند. اسیدیته و ساختار کاتالیزور Amberlyst-15 به طور قابل توجهی بر توزیع اجزای محصول، به ویژه تشکیل هیدروکربن های آروماتیک، با بازده نسبی ۲۷.۷۸٪ تأثیر گذاشت. مدل سینتیکی مرتبه اول نشان داد که تولید هیدروکربن های آروماتیک از قانون آرنیوس پیروی می کند.