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Seaweed biorefinery potential: Utilization of sulfated polysaccharide for chemical feedstock via pyrolysis

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Since the 20th century, different types of first- and second-generation biomass, including sugar crops, starch crops, vegetable oils, and lignocellulose (residue and by-products), have been developed and investigated. (Phakeenuya & Kitiborwornkul, 2024, Guo et al., 2015: 712-725, Phakeenuya & Kitiborwornkul, 2022: 1087-1101, Alalwan et al., 2019: 127-139) Transitioning from a conventional refinery to a biorefinery has prompted the search for biomass resources capable of generating both energy and valuable products, essential for the economic viability of the biorefinery. The consequent losses of food and fiber production due to issues surrounding conventional biomass have led to the exploration of marine resources, known as the third-generation biomass. (Jung et al., 2013: 182-190, Michalak, 2018: e288, Chowdhury & Loganathan, 2019: 39-44) Marine biomass, such as microalgae and seaweeds, is considered more sustainable and environmentally friendly because they can be grown in non-arable land, use less water, and capture carbon dioxide. (Baghel et al., 2015: 2436-2443, Konda et al., 2015: 1046-1056, Cesário et al., 2018: 798-817) However, investigations into seaweed for both energy production and valuable chemical products are limited.

Little attention has been given to research into new compounds derived from distinctive seaweed polysaccharides. While most reports on seaweed biorefining have concentrated on the production of bioethanol, hydrocolloids, or fertilizer and animal feeds, (Baghel et al., 2015: 2436-2443, Zaky et al., 2018: 12127) the extraction and/or production of valuable chemicals from seaweed polysaccharides are still in the early development stages. Consequently, the production of fine chemicals from seaweeds is intriguing and could enhance the value of a seaweed biorefinery.

Pyrolysis is a widely recognized method for breaking down biomass into valuable products, including bio-oil, bio-chars, and platform chemicals. (Bridgwater et al., 1999: 1479-1493, Yang et al., 2007: 1781-1788) The considerable interest in bio-oil is attributed to its practical applications, potentially containing diverse organic compounds convertible into valuable chemicals. (Yang et al., 2007: 1781-1788) To target these specific chemicals, addressing the challenge associated with the complex mixtures formed in bio-oil is crucial. Parameters influencing pyrolysis outcomes encompass the catalyst, feedstock, pretreatment method, and overall pyrolysis conditions. (Guo et al., 2015: 712-725) While some studies have investigated the thermal behavior of seaweed and its polysaccharides (e.g., carrageenan and alginate), (Wang et al., 2017: 373-383, Xue et al., 2017: 25253-25264, Kim et al., 2018: 60-69) there is a scarcity of research on the acid-catalyzed decomposition of this biomass. In contrast, the pyrolysis of terrestrial plants, such as cellulose, has undergone extensive examination. (Halpern et al., 1973: 204-209, Kawamoto et al., 2007: 127-133, Klepp et al., 2020: 38-53) The industrial-scale of acid-catalyzed pyrolysis of cellulose has been applied to produce levoglucosenone (LGO) and its reduced analogue, Cyrene™ (CircaGroup, 2023). These compounds are chiral platform chemicals and biorenewable solvents with wide application in the materials and pharmaceutical sectors. (Sarotti et al., 2012: 439-459, Comba et al., 2018: 590-604, Camp & Greatrex, 2022: 902239)

Numerous investigations have documented the thermochemical conversion of different seaweeds and their polysaccharides through conventional pyrolysis (Wang et al., 2017: 373-383, Jiang et al., 2019: 104680, Hu et al., 2021: 69-76) or microwave-assisted pyrolysis. (Bermúdez et al., 2014: 38144-38151, Budarin et al., 2011: 2330-2333, Gautam et al., 2019: 3009-3020) The predominant focus of these studies lies in the production of biochar and bio-oils, primarily for biofuel applications. Torres et al. (2019) concluded that the pyrolysis of seaweeds yields oils comparable to those from terrestrial biomass pyrolysis. (Torres et al., 2019: 335-388) Bio-oil, as commonly observed, contains aromatic compounds, (Budarin et al., 2011: 2330-2333) furfurals, (Jiang et al., 2019: 104680) ketones, (Bae et al., 2011: 3512-3520) and furan derivatives. (Gautam et al., 2019: 3009-3020)

The pyrolysis characteristics of polysaccharides from *Enteromorpha clathrata* (green seaweed) and *Sargassum fusiforme* (brown seaweed) were investigated using thermogravimetric-mass spectrometry (TG-MS) and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). (Wang et al., 2017: 373-383) *E. clathrata* polysaccharides primarily comprise glucan, xylan, and glucuronide-sulfate-rhamnose, while *S. fusiforme* is mainly composed of uranic acid, sulfate group-fucose, and polysaccharide galactose. The primary pyrolysis products from *E. clathrata* and *S. fusiforme* polysaccharides are furans and esters, respectively.

In their research, Jiang et al. (2019) conducted catalytic pyrolysis on sulfated polysaccharide extracted from *Enteromorpha clathrata* using Py-GC/MS over ZSM-5 catalysts at a temperature of 550 °C. (Jiang et al., 2019: 104680) Furfural emerged as the predominant product in the bio-oil, constituting 50.3%, along with other furan-containing compounds. The mechanism aligns with the findings of Wang et al. (2017), suggesting that volatile compounds result from the decomposition of glucuronic acid and rhamnose units. The authors verified that the ZSM-5 catalyst played a role in promoting hydrodeoxygenation reactions, consequently modifying the bio-oil and enhancing 5-methylfurfural production.

Recent studies on pyrolysis of carrageenans, main polysaccharides of red seaweeds, have been reported. (Rodiahwati et al., 2023: 105904, Rodiahwati et al., 2023: 101576) The authors investigated three different carrageenans in the H_2SO_4-catalyzed pyrolysis in polyethylene glycol (PEG). The use of PEG as a reaction medium promotes the carbocation rearrangement and allows a higher loading of carbohydrates, 20% w/w, (Rodiahwati et al., 2023: 105904) compared to those in using tetrahydrofuran (THF) 1% w/w. (He et al., 2017: 3642-3653) The findings show that platform chemical LGO was the major product follow by furfural, the general product from biomass pyrolysis. Although the yields from these studies are still lower compared to LGO from cellulose pyrolysis, this research is the first study reported LGO production from acid-catalyzed pyrolysis of carrageenan in PEG. Hence, this has given insight into utilizing red seaweeds for the production of chemicals as a support of future seaweed biorefinery and coalign with the concept of circular, bio and green economy (BCG economy) (Kitiborwornkul & Sriariyanun, 2024).

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