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Reactive Extrusion of Lignocellulosic Biomass to Produce Biopolymer Monomers using High-Energy Radiation and Catalytic Acids

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Reactive Extrusion of Lignocellulosic Biomass to Produce Biopolymer Monomers using High-Energy Radiation and Catalytic Acids

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Abstract: The increasing prevalence of bio-based and biodegradable plastics as an alternative to traditional plastics derived from crude oil is a noteworthy trend. Polybutylene succinate (PBS), a plastic produced from succinic acid, is among the promising materials for the future. However, the production of bio-based succinic acid through biotechnical processes in controlled environments presents challenges. This process leads to increased costs and is currently not economically competitive compared to crude oil-based succinic acid production. In addition to succinic acid, levulinic acid is another monomer produced in the same process. A novel approach to the digestion of biomass has been developed to address the issue of biotechnological production of bio-based platform chemicals. This innovative process employs microwave radiation, pressure, and temperature to convert wood residues into succinic acid and levulinic acid. Various catalyst concentrations and biomass ratios were tested in a batch process, with high-pressure liquid chromatography (HPLC) and liquid chromatography–mass spectrometry (LC/MS) analyses revealing the formation of succinic acid, levulinic acid, formic acid, and 2-oxoglutaric acid. The results demonstrate that microwaves combined with a metal salt catalyst can be used to produce platform chemicals from lignocellulosic biomass. To further advance the continuous production of PBS, a twin-screw extruder was modified and adapted after the successful results obtained from the batch processes. This setup enables additional experiments to evaluate the transferability of batch process results to continuous reactions, facilitating the scale-up and the economic viability of the overall PBS production process in the future.

Keywords: Succinic Acid, Levulinic Acid, Biopolymer, Microwave, Wood

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Introduction

The annual production of plastics has expanded globally. In 2019, the volume was around 368 million tons [1]. A majority of these are derived from fossil raw materials. The bio-based plastics sector at present represents a niche, but it offers the advantage of reducing greenhouse gas emissions, specifically carbon dioxide [2], which is crucial in achieving temperature targets to combat climate change [3]. Bio-based plastics are primarily produced from plants containing carbohydrates that are fermented and dissolved by bacteria and yeasts in batch processes [4]. The resulting platform chemicals are subsequently separated through complex procedures [5]. The conversion process in these bioreactors is intricate. The biomass used as first-generation feedstock is competing with food production, as it can be used for sustenance, but it also occupies agricultural land and water [6]. The environmental impact of plastics is a pressing social issue, as plastic particles accumulate in the environment over a relatively short time due to the fact that a large portion of them biodegrade very slowly [7]. Biodegradable plastics offer the advantage of being mechanically broken down and disintegrating over time without creating microplastic. One example of a bio-based and biodegradable plastic is polybutylene succinate (PBS) [8]. The synthesis of PBS requires the platform chemical succinic acid. A newly developed process at the Technical University of Rosenheim enables the production of platform chemicals from lignocellulosic biomass through the utilization of catalysts, pressure, temperature, and microwave irradiation. This paper examines the batch process and the construction of a continuous production demonstrator on a laboratory scale.

Materials and Methods for Batch Process

Materials

Spruce wood chips (*picea abies*) from a local sawmill were used. A metal salt catalyst with a purity of over 95% was provided by VWR. The following chemicals were used for standard chemical analysis (Table 1). Hydrochloride Acid and Nitric Acid were used to clean the microwave digestion vessels.

Table 1. Raw Materials.

Chemicals	Purity in %	Producer
Levulinic Acid	98.0	Sigma Aldrich
Formic Acid	99.0	VWR
2-Oxoglutaric Acid	98.0	Sigma Aldrich
Succinic Acid	99.6	VWR
Hydrochloric Acid	30.0	Merck
Nitric Acid	69.0	Roth

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Devices

A HAVER CPA 2-1 particle sizer from Haver & Boecker was used to determine the grain size of the spruce chips. The analysis of the products after hydrolysis of the wood was carried out using an HPLC Series 200 from Perkin Elmer and an LC/MSD iQ from Agilent Infinity Lab. The column used for the HPLC and LC/MSD is an Aminex® HPX-87H from Bio-Rad. The wood was hydrolyzed in a Multiwave 5000 with rotor (20SVT50) and Teflon pressure vessels (SVT50) from Anthon Paar.

Hydrolyses

The hydrolysis of the wood particles was carried out at a temperature of 200°C with a heating time of 10 min at a pressure of 1.5 MPa. The samples were stirred at the "high" level during the test. The exposure time of the samples was varied between 2 min, 5 min, and 10 min and cooled down to 65°C after microwave irradiation. Each test series comprised four samples.

A catalyst solution was mixed. A concentration of 1% mass was used for preparing a catalyst solution. This corresponds to 1.0 g metal salt catalyst per 100.0 g distilled water. Higher concentrations were also tested for samples (6 ml) with 2.0 g and 5.0 g catalyst. The biomass loading is calculated using the following formula:

$$Biomass\ loading\ in\ \% = \frac{0.20\ g\ Wood}{\mathrm{y}} \qquad 1)$$

y = amount of catalyst solution in g

Table 2 shows the concentrations of wood and water with the calculated biomass loading for each reaction time.

Table 2. Wood, Time, and Catalyst.

Reaction Time in min	Spruce in g	Catalyst Solution in g	Biomass loading in mass %
2.0	0.20	2.0; 4.0; 6.0	10.0; 5.0; 3.3
5.0	0.20	2.0; 4.0; 6.0	10.0; 5.0; 3.3
10.0	0.20	2.0; 4.0; 6.0	10.0; 5.0; 3.3

After each cycle, the reaction vessels were subjected to a cleaning program with distilled water, hydrochloric acid and nitric acid at 180°C in the microwave for 20 min.

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Analytics

HPLC and LC/MS analysis were used to analyze the chemicals produced. The samples were diluted to 1:20 with distilled water before analysis. The method for the HPLC was isocratic with an analysis time of 25 min, a temperature of 35°C, an inlet volume of 20 µl with a flow rate of 0.6 ml/min and a mobile phase of 0.005 N H_2SO_4. The UV/VIS detector was set to 210 nm.

For the LC/MS analysis, an analysis time of 15 min, and an injection volume of 20 µl at a flow rate of 0.6 ml/min was set. The mobile phase is a 0.5% v/v formic acid. The scan range is 50-450 m/z, the gas temperature is 285°C, and the gas flow is 13 L/min. The fragmentor was operated at 75 V and the capillary at 3 kV.

Results Batch Process

The particles are on average 1.8 mm in size with a maximum size of 8 mm.

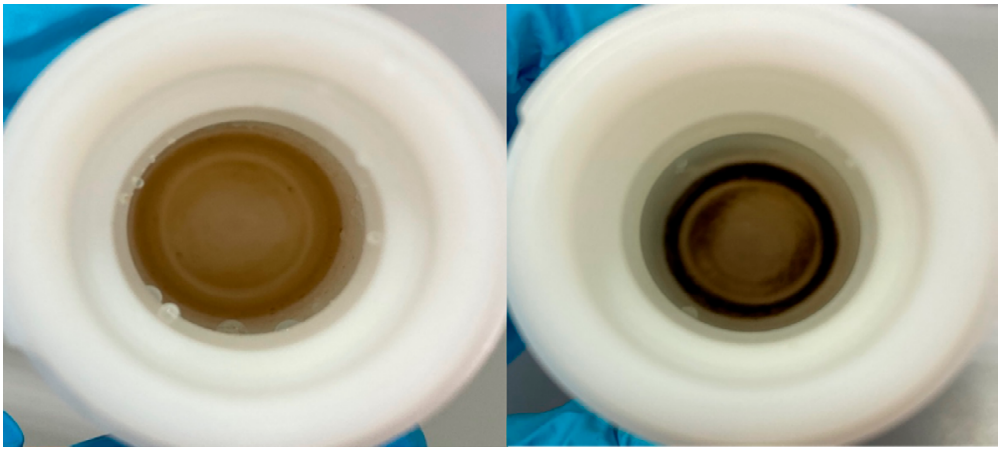

Figure 1. Solution after microwave radiation. 2 min (left), 10 min (right).
6 ml of catalyst solution with 1% metal salt catalyst and 0.2 g of wood.

After placing the sample in the microwave reactor for an extended period of time, a brown sediment formed, as compared to a 2-min irradiation where a transparent yellow solution was produced, as illustrated in Figure 1.

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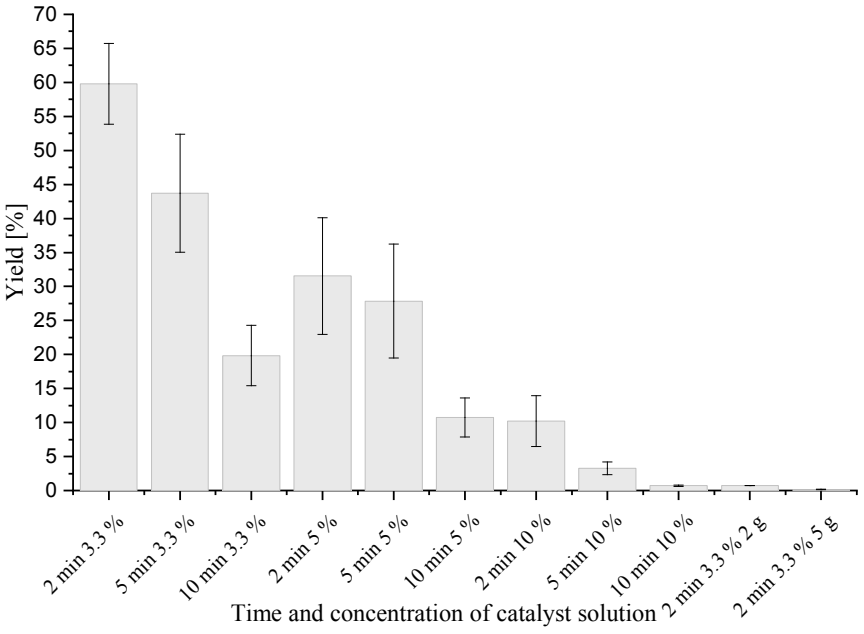

Figure 2. Yield of succinic acid.

The optimal succinic acid yield of 59.8% (±5.9%) was obtained at a biomass loading of 3.3% and a duration of 2 minutes, as seen in Figure 2. When the exposure time was increased, the yield significantly decreased, even with the same biomass loading. As the biomass increased, the yield of succinic acid decreased.

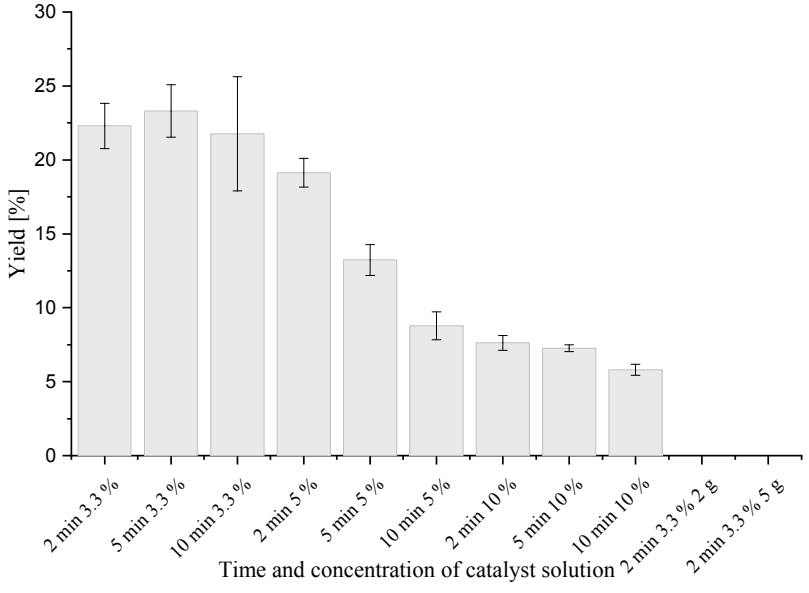

Figure 3. Yield of levulinic acid.

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The output of levulinic acid diminished as the quantity of biomass expanded. The greatest concentration was attained at an irradiation of 5 minutes, which amounted to 23.3% (±1.8%), as illustrated in the bar graph in Figure 3. As the biomass loading increased, the concentration of the catalyst decreased.

In addition to succinic acid and levulinic acid, the production of smaller quantities of formic acid and 2-oxoglutaric acid was also observed. However, with higher amounts of catalyst, the yield of succinic acid and levulinic acid decreased, while the yield of 2-oxoglutaric acid increased. At 2 minutes, a biomass loading of 3.3% and a catalyst concentration of 5% yielded 11.2% (±1.5%).

Materials and Methods for Continuous Process

The outcomes of the laboratory experiments for the production of platform chemicals from lignocellulosic biomass were obtained via a batch process. The subsequent development step involves the design and construction of a laboratory-scale system for the continuous production of platform chemicals. To this end, a twin-screw extruder was modified. The extruder is two meters long and has a screw length of 80 D. Solid-state generators were adapted to the extruder at regular intervals along the conveying length to establish a lengthy reaction zone. A suspension of wood particles and water is fed into the twin-screw extruder by means of a pump. A separate dosing pump is used to administer the catalyst into the extruder after the wood particles. After the suspension has passed through, an aqueous solution containing the dissolved platform chemicals should be present at the outlet of the extruder. Excess water is recycled back into the process through evaporation and a heat exchanger, which also serves to conserve energy. The side view of the pilot machine is illustrated in Figure 4 below.

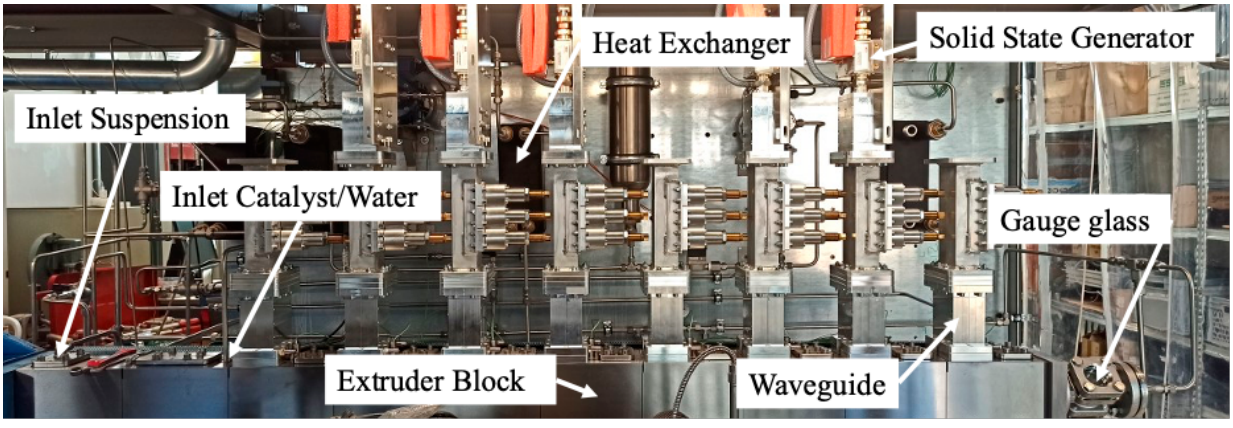

Figure 4. Modified Extruder with different components.

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Conclusion

The research studies presented in this paper reveal the potential for producing platform chemicals through the degradation of wood on a laboratory scale. Utilizing microwaves in conjunction with metal salt as a catalyst, along with pressure and temperature, it is possible to break down wood and produce levulinic acid and succinic acid. The highest yield was achieved with a biomass loading of 3.3% and a process time of 2 minutes. The combined yield surpassed 80%, which is higher than the cellulose (43%) and hemicelluloses (35%) content of spruce wood. This exceptional yield can be attributed to the inherent inhomogeneity of wood as a natural product. The samples used in the study were relatively small, weighing 0.2 grams, and may have exhibited local variations in their compositions of celluloses, hemicelluloses, and lignin. Further experiments with a larger number of samples will be necessary to determine the optimal compositions for achieving the highest possible rates of platform chemicals.

In addition, a pilot plant for the continuous production of platform chemicals from wood residue has already been constructed. The next step is to operate and optimize the process parameters. Initially, this will involve using process parameters from batch processes. The continuous process allows the production of larger quantities of chemicals, which will be analyzed and used to optimize the process in subsequent steps.

Acknowledgments

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