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# Hydrothermal treatment for enhancing oil extraction and hydrochar production from oilseeds

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ABSTRACT

A novel integrated oil extraction process that includes hydrothermal pretreatment and oil extraction (HPOE) from whole oilseeds followed by hydrothermal carbonization (HTC) of the extracted seedcake to hydrochar was developed. Five different types of oilseeds including cotton-, flax-, mustard-, canola-, and jatropha seeds were used in the study. The seeds were subjected to hydrothermal pretreatment in the range of temperatures from 120 to 210 °C for 30 min. Oils were extracted from the pretreated seeds using *n*-hexane in a Soxhlet apparatus for 120 min. The crude oil yields from the pretreated seeds at 180 °C and 210 °C were significantly higher (up to 30 wt%) than those from the respective untreated ground seeds. The seedcake after oil extraction was subjected to HTC at 300 °C with the recycled aqueous phase collected from the pretreatment step. The produced hydrochar had higher heating value of 26.5 kJ/g comparable to that of bituminous coal. BET surface area and pore volume analysis showed that the pretreated seeds had larger surface area and pore volume/size than the respective raw seeds, which resulted in better extractability of oil, shorter extraction time, and overall efficiency of HPOE process. Analyses of the crude oil did not show significant signs of degradation after the hydrothermal pretreatment of oilseeds. The study is the first of its kind where integrated oil extraction and hydrochar production from oilseeds have been studied with the objective of minimizing feedstock preparation and maximizing oil extraction and overall energy conversion using environmentally benign hydrothermal processes.



## 1. Introduction

Oilseed is a valuable source of oil that can be readily extracted and used in a number of applications. The oil content of various oilseeds typically accounts for 15–50 wt% the total seed mass. Oilseeds are primarily used for the production of vegetable oil and oilseed meal for food and animal feed. Oils of non-food quality are being envisioned as a valuable renewable feedstock for producing biodiesel or other alternative fuels that provide national energy security, reduce impact on the environment, and stimulate rural economic growth without affecting the food market [1]. The advantages of using oils from non-food-based resources for biofuel production include their availability, high energy density, biodegradability, near-zero aromatic and sulfur content, and non-toxicity. The liquid nature of the oils makes them a convenient feedstock for transportation and processing.

One of the most costly stages in the production of fuels from oil-based feedstock is the extraction and purification of oils derived from the biomass [2]. Therefore, developing efficient and robust oil extraction methods is a major challenge facing biofuels industries. A variety of methods of extracting oils from oilseeds exist to date. The oils are typically extracted using either mechanical pressing or different organic solvents. Mechanical extraction is simple but leaves behind up to 5–6 wt% unextracted oil [3]. Solvent extraction provides better oil recovery but requires thorough preparation of the feedstock including drying, cleaning, dehulling, conditioning, flaking, cooking/tempering, and pre-pressing [4]. A number of solvents can be used for oil extraction from oilseeds. However, *n*-hexane is the only solvent that has been used on a commercial scale and has demonstrated high efficiency for extraction of neutral lipids (triglycerides) from various oil crops [5]. For these reasons, *n*-hexane was employed as a solvent for extraction of oils in this study.

Hydrothermal pretreatment of oilseeds might be a promising

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way of increasing the extractability of oils without prior grinding and/or dehulling oilseeds [6]. Processing biomass under hydrothermal (subcritical water) conditions is considered an efficient and environmentally benign method that capitalizes on the extraordinary properties of water as a solvent and reaction medium. In subcritical water-based processes, water is kept in a liquid phase by applying pressure greater than the vapor pressure of water. In this way, the latent heat required for phase change of water is avoided, which requires less energy than steam generation [7].

A few types of oilseeds with different morphologies were used in this study. The hydrothermal pretreatment of the oilseeds was performed in a wide range of subcritical temperatures in order to determine the optimal conditions of the HPOE process. The process was aimed at maximizing extractability of oils mostly from inedible/non-food quality crops for biodiesel production. HPOE can also be used for extraction of oils from edible crops under milder conditions in order to minimize changes of the oil quality. In this case, carbonization of the extracted seedcake is not necessary; instead, it can be used as an animal feed. However, additional research is required for using HPOE for food applications.

Hydrochar is a valuable co-product that can be used as solid fuel, co-fired with coal, or as a soil amendment agent for growing oil crops. After a simple activation step, it can also be used for industrial wastewater treatment [8]. For some types of oilseeds like jatropha, which are highly toxic, utilization of the seedcake poses a challenge. Therefore, hydrochar production can be a feasible option that adds value to the overall process. Shackley et al. estimate the cost of hydrochar produced from green waste from $91 to $329 per ton depending on the type of storage and production facility [9].

The focus of this study was to develop and investigate an integrated oil extraction process that employs HPOE of the whole oilseeds followed by HTC of the extracted seedcake. The schematic of the integrated process is shown in Fig. 1. To the best of our knowledge, no research has been done on oil extraction and hydrochar production from hydrothermally pretreated seeds up to date [10].

The novelty of the proposed process are: (i) using environmentally benign hydrothermal processes for maximizing oil yield without feedstock preparation, (ii) studying the effect of hydrothermal pretreatment on the oil yield from oilseeds with different morphologies and in a wide range of temperatures (120–210 °C), (iii) integrating oil extraction with hydrochar production, which increases the overall energy conversion of the feedstock.

The objectives of this study were as follows: (i) to evaluate the effect of hydrothermal pretreatment of oilseeds on the crude oil yields in the range of temperatures from 120 to 210 °C, (ii) to study the kinetics of Soxhlet extraction from both ground raw and whole pretreated seeds, (iii) to compare the composition and quality of the extracted crude oils, (iv) to utilize the extracted seedcake for hydrochar production using the aqueous phase obtained after the pretreatment step, and (v) to develop the overall mass balance of the HPOE process and evaluate its energy requirements.

The integrated process provides several major advantages over conventional processes including better extractability of oil, shorter extraction time, tolerance to high moisture content of the feedstock, avoidance of preparation stages, and utilization of extracted seedcake for hydrochar production. The proposed HPOE process can potentially be integrated with biodiesel productions.

## 2. Materials and methods

### 2.1. Materials

Five types of oilseeds including cotton-, flax-, yellow mustard-, canola-, and *Jatropha curcas* seeds were purchased and used as received. The cottonseeds were obtained from a local farm in Virginia (white fuzzy seeds), the flax-, mustard-, and canola seeds were purchased from Superior Nut Company, Cambridge, MA, Penzeys Spices, Wauwatosa, WI, and Seedland, Wellborn, FL, respectively. *Jatropha curcas* seeds were purchased from Tree Seeds Plus eBay store. *n*-hexane 95% (Optima), methanol 99.9% (Optima LC/MC), ethanol 190 proof (95%), sodium hydroxide ≥ 97% (Pellets/Certified ACS), potassium hydroxide ≥ 95% (Pellets/Certified ACS), dichloromethane 99.5% (Pfaltz & Bauer Inc.), 2,2-diphenyl-1-picrylhydrazyl (95%), gallic acid (Powder/Certified), toluene ≥ 99.5% (Certified ACS) were purchased from Fischer Scientific USA and used as received.

For oil quality analysis, MXT-WAX capillary column (30 m × 0.53 mm × 1 μm) and FAME standards #1 and #3 containing 20 wt% methyl esters of caprylic (8:0), capric (10:0), lauric (12:0), myristic (14:0), palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3) acids (20 wt% each) were purchased from Restek, Bellefonte, PA. Rtx-65TG capillary column (30 m × 0.25 mm × 0.1 μm) was purchased from Restek, Bellefonte, PA. SCOTTY gas calibration standard containing 50 wt% $H_2$, 10 wt% $CH_4$, 10 wt% CO, 20 wt% $CO_2$, 5 wt% ethylene, and 5 wt% propane was purchased from Sigma–Aldrich.

### 2.2. Experimental part

#### 2.2.1. Hydrothermal pretreatment of oilseeds

The seeds for hydrothermal pretreatment experiments were used as received (without dehulling and grinding). All the oilseeds were dried for 24 h in an oven at 65 ± 3 °C, packed in plastic bags, and stored in a dark and dry place at room temperature before being used. The moisture content of the seeds was determined with a moisture meter Denver Instrument IR 35 by drying them at 105 °C to constant weight. The moisture of oilseeds was ≤1 ± 0.2 wt%.

The temperatures between 150 and 200 °C are typically used for hydrolysis of different types of biomass. Subcritical water treatment at the above temperatures was successfully employed for improving lipid extraction from yeast, activated sludge, and some oilseeds [6]. We used a broader range of pretreatment temperatures and longer times because oilseeds with very different morphologies were used as a feedstock in the study.

Hydrothermal pretreatment of the seeds was carried out in a 500 mL batch reactor equipped with a Parr 4848 controller at 120 ± 1, 150 ± 1, 180 ± 1, and 210 ± 1 °C (the respective autogenous

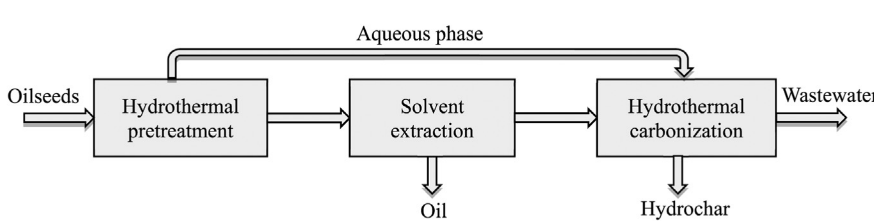


**Fig. 1.** Schematic of the integrated HPOE process.