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Isolation, characterization and evaluation of photochemical potential of rice husk-based furfural via continuous flow reactor

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ABSTRACT

Rice husk is an abundant agricultural waste containing about 120 g pentosan per kilogram of dry husk; a precursor for furfural production. Furfural, among the furan-based compounds, shows interesting properties as a building-block or industrial solvent in the production of higher-valued co-product chemicals. In our study, we isolated furfural from rice husk using known acid-catalyzed methods (microwave, reflux and autoclave) and compared their performance in terms of percentage furfural yield. Relatively higher furfural yield ≤68% was obtained using microwave-assisted method. We developed a simple and innovative quartz flow capillary microreactor to investigate the photochemical potential of sunlight as a clean energy source in transforming furfural into 5-hydroxy-2-(5*H*)-furanone; a versatile synthon in organic synthesis. Excellent furanone yield (84%, RSD = 0.78–4.67) was obtained after 6 h of sunlight irradiation in presence of Rose Bengal photosensitizer.

1. Introduction

Ecological sustainability concern and surging crude oil prices have amplified industrial interest for renewable biomass resources [1]. Of the various biomasses with abundant and renewable energy sources, rice husk is not only a cheap potential source of energy, but also a value-added by-product [2]. Its annual worldwide output is in million tons [3], and its major components are hemicellulose (19%), cellulose (40%), silica (17%) and lignin (16%) [4]. Agricultural waste-based lignocellulosic materials rich in pentosans have generally been preferred for producing value-added chemicals [5] since they are homogeneous and readily available in large quantities from cheap sources [6]. Biomass resources are a perfect choice to replace the petroleum feedstock [7]. They are even considered viable options for improving energy security and reducing greenhouse-gas emissions thus addressing the recurrent treatment challenges of waste streams from process plants [8]. However, their effective utilization is limited by the quest in developing inexpensive processing methods that are capable of transforming the abundantly available carbohydrate moieties into value-added chemicals [9]. Recently, furfural has received renewed attention as a potential renewable platform for the production of biochemicals and biofuels [10]. Furfural (2-furaldehyde) is a versatile furan platform comprised of a hetero-aromatic furan ring and an aldehyde group and is reported to be the sole precursor for compounds containing furoyl (furoyl glycine and 2-furoylchloride), furyl (furanones and furans), and furfurylidene radicals [5]. It is asserted to be among the top 30 high-value bio-based chemicals [11], and its demand is greatly felt in fields such as petrochemical refining, agrochemical, pharmaceutical and plastics industries [12]. The properties of furfural are summarized in the Table 1.

Furfural production involves both acidic hydrolysis and dehydration through either one or two stage process using either one or multiple reactors [4,5] as shown by the reaction Scheme 1. In most research reports, a two-stage process is utilized since it generates higher furfural yield [13].

The currently used batch and continuous furfural production processes are energy intensive, expensive, environmentally unfriendly and cause acid wastes [5]. Hence, the recent trend in furfural research is geared towards novel production processes that are both inexpensive and environmentally appealing. The techniques of supercritical fluid extraction [15], pressurized solvent extraction [16] and microwave-assisted extraction method [5] have been accepted as novel methods in furfural production.

Conversely, the use of abundant sunlight as a clean source of energy to initiate chemical transformations has attracted the attention of synthetic organic photochemists, since a variety of photoreactions high in selectivity, chemical yields and photon

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Table 1
Some general furfural properties (Dontulwar et al. [26]).

Molecular weight	96.1
Freezing point (°C)	−36.5
Boiling point (°C)	161.7
Density at 25 °C	1.5
Viscosity at 25 °C	798.2
Critical pressure (psi)	398.2
Critical temperature (°C)	397.4
Heat of combustion at 25 °C (kcal/g mol)	−560.3
Heat of formation (liquid at 25 °C) (kcal/g mol)	−49.2
Heat of fusion (kcal/g mol)	3.43

efficiencies are generated [17]. Moreover, sunlight is a cheap, environmental friendly, plentiful and continuous renewable source of clean energy. However, despite these significant merits, organic synthesis still remains highly resource- and labor-intensive [18]. Recently, microphotochemistry has been utilized in synthetic organic chemistry since it combines the advantages of miniaturized microflow systems with organic photochemistry [19]. The continuous removal of the product mixture from the irradiated area reduces secondary photoreactions, whereas the thin reaction channels enable efficient penetration of light through the reaction mixture (as dictated by the Beer–Lambert law) [20].

To the best of our knowledge, there have been no studies conducted till date to fully evaluate the photochemical utilization of furfural from rice husk via continuous flow microreactor system. In the present work, furfural was isolated from rice husk using three known acid catalyzed methods and their efficiencies compared in terms of percentage furfural yields. A simple flow quartz capillary microreactor was developed and used to investigate the quantitative synthesis of 5-hydroxy-2-(5*H*)-furanone from furfural using organic dyes as singlet oxygen photosensitizers and sunlight as the energy source. Organic dyes are reported to be cheap, easy to prepare, more environmentally friendly and present a practicable alternative to inorganic photocatalysts [21]. The application of light-induced reactions in continuous flow microreactors combines the advantages of microreactor technology with sunlight photons as clean and traceless reagents [22]. In addition, microreactors offer higher spatial illumination homogeneity and better light penetration throughout the entire reactor [23].

2. Method

2.1. Chemicals

The chemicals employed in this work were of analytical grade and were used as purchased. Ethanol, hydrochloric acid (37%) and Rose Bengal (RB) were purchased from Sigma–Aldrich Canada Ltd. (Oakville, Canada). Acetic acid (99.7%) and methanol were secured from Fisher Scientific (Pennington, NJ). The water used in all treatments and analyses was high purity Milli-Q water (18 MΩ) obtained from Milli-Q water purification system (Millipore, Milford, MA).

2.2. Biomass

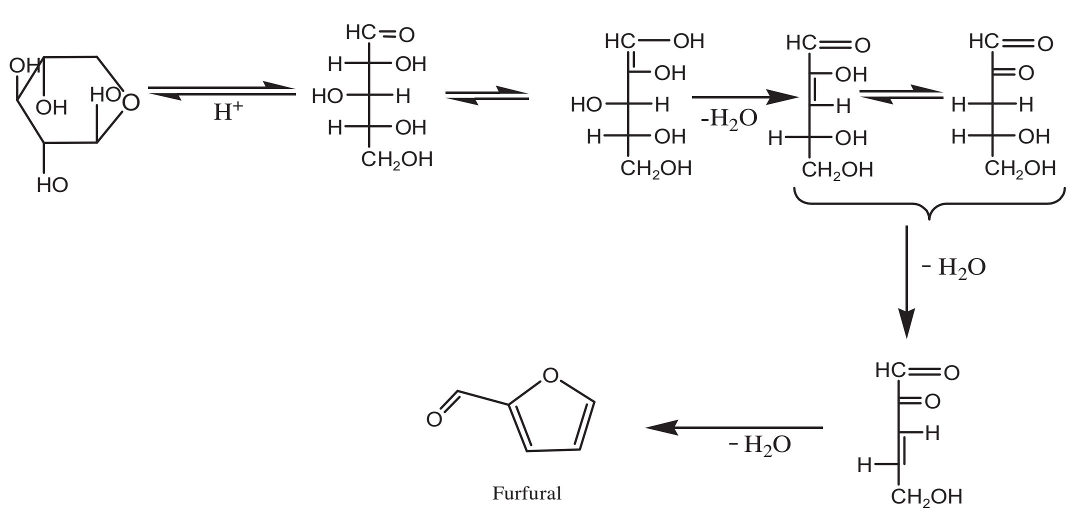
Rice husk used in this study was provided by Chirackal agro mills Chirackal modern rice mill (Kerala, India). They were washed thoroughly with distilled water in a 2 L measuring cylinder, dried at 105 °C for over 12 h and then pulverized to pass through a 1 μm mesh screen for further use.

2.3. Acid-catalyzed conversion processes of rice husk to furfural

The acid-catalyzed conversion of rice husk into furans was evaluated using three different isolation methods namely; a two-stage process involving microwave-assisted isolation [24], reflux method reported by Ong and Sashikala [16] and autoclave extraction method reported by Suxia et al. [4]: as described.

2.3.1. Autoclave-assisted conversion method

A sample of pulverized rice husk (8.0 g) and 100 mL H_2SO_4 (1.0 M) were mixed and packed into 500 mL stainless steel autoclave with a Teflon inner lining for acid hydrolysis. The packed vessels were sealed at both ends with circular cellulose filters and end caps, and then placed into a pre-heated oven for 7 h to hydrolyze pentosan present in the rice husk. After the preset time, the autoclave was removed and cooled down to room temperature. The resultant solid–liquid mixture was then filtered. A portion of the filtrate (50 mL) was further dehydrated by mixing it with 3.0 g of functionalized solid acid catalyst (SBA-15) into the autoclave followed by simultaneous addition of 150 mL of toluene. At the end of the reaction, the rice husk residues were filtered off leaving behind a two-layered mixture that was later separated



Scheme 1. Production of furfural from pentose sugars [14].