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Fodder radish seed cake pyrolysis for bio-oil production in a rotary kiln reactor

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ABSTRACT

Fodder radish seed cake (FRSC) was pyrolyzed in a rotary kiln reactor at different rotation speeds (0, 3 and 6 rpm) and inert gas flow rates (0.25, 0.75 and 1.25 L/min). Pyrolysis of the bran (oil-free FRSC) were also carried out to investigate the effect of residual oil present in the FRSC. The experiments showed that the optimal rotation speed for bio-oil production is 3 rpm, with a bio-oil yield of 60.99 wt.%. The experiments carried out at different inert gas flow rates showed an increase of bio-oil yield at 1.25 L/min (63.22 wt.%). The residual oil in the FRSC increased bio-oil yield, since FRSC bran (oil-free) pyrolysis presented a bio-oil yield of 49.34 wt.%. The bio-oils obtained from FRSC pyrolysis, as well as its bran, presented distinct chemical composition. FRSC bio-oil presented, besides aromatics, amines, amides, and nitriles (nitrogen containing functional groups). The bio-oil obtained from FRSC bran pyrolysis presented higher aromatics content than the bio-oil from FRSC, with lesser amines content and absence of nitriles. The bio-oil obtained from FRSC pyrolysis at 3 rpm was the one that presented the more adequate physicochemical properties for use in industry and for energy production. Due to the composition, the bio-oils can be used as fuel, to obtain chemicals and as a feedstock for gasification.

1. Introduction

Fodder radish (*Raphanus sativus* L.) is an angiosperm belonging to the *Brassicaceae* family. The high oil content in its seed (from 30 to 50 wt.%) permit to use it as feedstock to produce biofuels (biodiesel). Its applications range from forage and crop rotation to a source of vegetable oil and biomass for many uses, being its most prominent use in biodiesel production, from the seed oil [1,2]. Fodder radish has an average productivity of 3000 kg/ha of dry mass (in relation to aerial part). Seed production is around 800 to 1200 kg/ha, depending on the climate and cultivation nutritional state. The oil is industrially obtained by pressing of the seed in a roller extractor, the oil is obtained and separated and occurs generation of a waste, the bagasse of kneaded seed (cake) [3]. Seed oil is composed by a mixture of saturated and unsaturated fatty acids, whose composition depends on plant genetics, nutritional conditions, climate, soil type and presence of diseases, but the major components are oleic and erucic acids [4].

Fodder radish seed cake (FRSC) is the waste (cake) of the fodder radish seed after the pressing process to extract its oil. In the view of the fact that the extraction process is inefficient, FRSC still has a substantial quantity of residual oil. FRSC can be used as a feedstock in thermochemical processes (pyrolysis) in order to obtain a bio-oil with distinct characteristics from lignocellulosic biomasses, composed basically by cellulose, hemicellulose and lignin [1,5]. FRSC has high protein content, being attractive to use this biomass in animal feeding, though the presence of oil is a problem to use the material this way. Literature present studies characterizing FRSC and its bran (cake with the residual oil removed) in order to verify its use in cattle and fish feeding [6,7].

Literature cites works using rapeseed seed cake (*Brassica napus*), which belongs to fodder radish botanical family. Ucar and Ozkan [8], pyrolyzing rapeseed seed cake in a fixed bed reactor at temperatures between 400 and 900 °C, obtained maximum bio-oil yield at 500 °C, whose fraction bio-oil plus water corresponded to 58.59 wt.% and the main organic constituents of the obtained bio-oil were oleic acid, 1H-indole and 2,3,5-trimethoxy-toluene. Smets et al. [9], working with rapeseed seed cake in an auger reactor at temperatures between 350 and 550 °C, obtained higher bio-oil yield at 550 °C, with value of 42.1 wt.%, being oleic acid the main organic constituent of the organic phase, followed by erucic acid. Smets et al. [10], performing slow pyrolysis of rapeseed seed cake at 550 °C using diverse catalysts, obtained higher bio-oil yield without use of catalyst (47.1 wt.%). The main constituents of liquid organic fraction were oleic, linoleic and palmitic acids.

Bubbling fluidized bed (BFB) and circulating fluidized bed (CFB) are the most used reactors in fast pyrolysis [5,11,12,13]. Literature cites the

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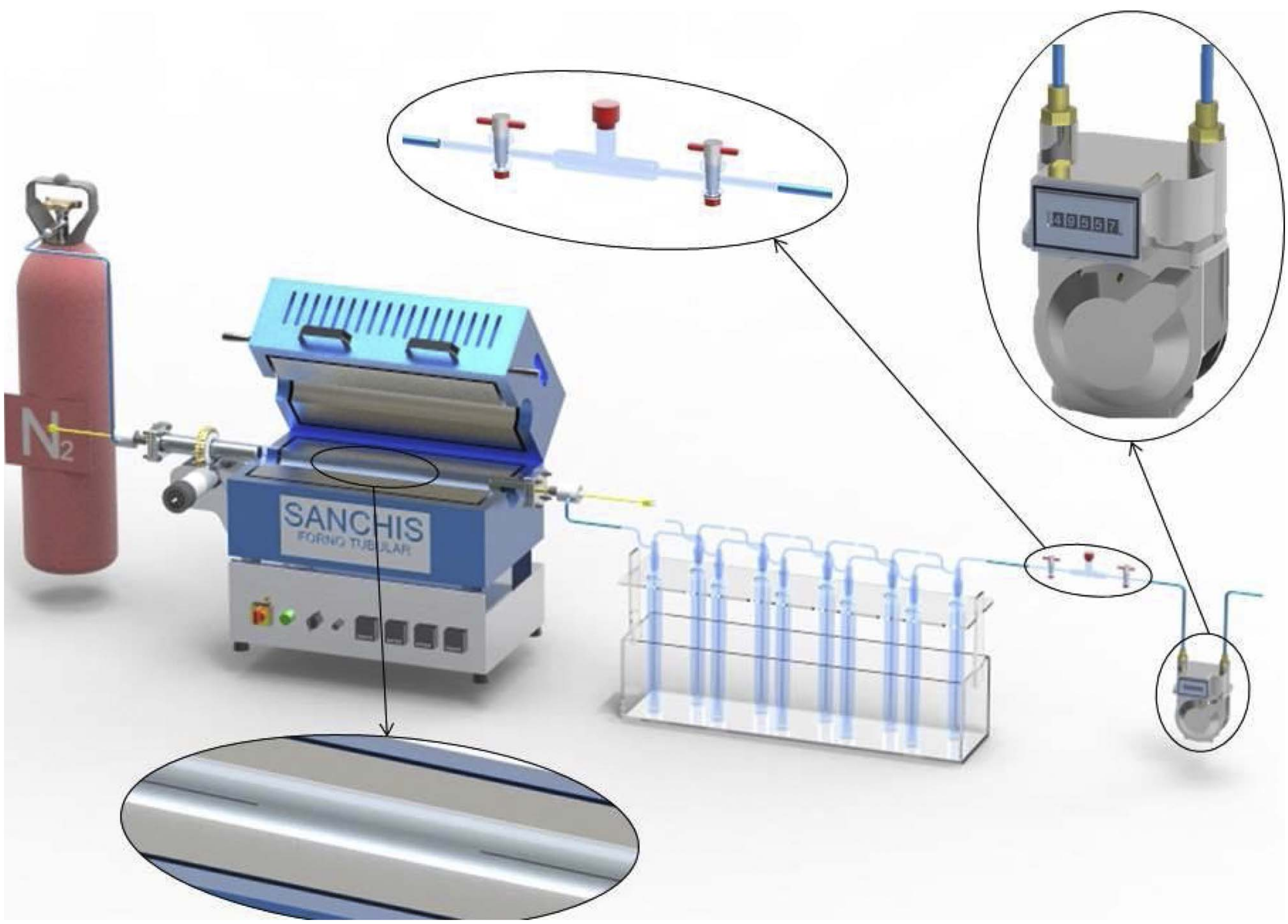

Fig. 1. Scheme of the pyrolysis system used in the experiments.

use of many other types of reactors, both for slow and fast pyrolysis [5,12,14]. The rotary kiln is widely employed in industry, with varied dimensions and a wide range of applications, being much employed in combustion and calcination (cement industry). In pyrolysis, this reactor shows advantages comparatively to other reactors in biomass processing. The rotary kiln allows the use of solid biomass of several shapes and sizes and the system can operate both in batch and in continuous mode, besides being of more simple construction and operational control, instead of BFB and CFB reactors, which demand a strict control [15,16,17]. As well as in fluidized bed reactors, the pyrolytic vapors are removed from the rotary kilns by the inert gas flow rate (in general, nitrogen gas is used). The residence time of the pyrolytic vapors is associated to the volumetric flow rate of inert gas. To obtain higher bio-oil yields, is recommended a residence time smaller than 2 s in BFB and CFB reactors [5].

Studies has been conducted with rotary kilns for the pyrolysis of different materials. Zhengzhao et al. [18] carried out pyrolysis experiments of mud of oil fields in a rotary kiln at 5 rpm. The results showed bio-oil yields of 10 wt.% at 480 °C, 13 wt.% at 520 °C, 24 wt.% at 550 °C and 19 wt.% at 580 °C. Cha et al. [15] conducted experiments in a rotary kiln coupled to a screw feeder to pyrolyze sand impregnated with bitumen. Authors evaluated the following operational conditions: final temperature of 500 °C, inclination of 2.5°, rotation speed of 3 rpm, feed rate of 10 kg/h and inert gas flow rate of 2.2 m^3/h. The authors reported bio-oil yield of 52.8 wt.% at 500 °C.

Rotary kilns are also being used in biomass pyrolysis. Li et al. [17] conducted pyrolysis experiments of various materials, among then wood chips, in a rotary kiln at temperatures from 550 to 850 °C. At final temperature of 550 °C, bio-oil yield for wood chips was near 50 wt.%. With increase in final pyrolysis temperature there was a reduction of bio-oil yield.

Kern et al. [19] carried out pyrolysis experiments of wheat straw in a rotary kiln. At final temperature of 500 °C bio-oil yield was 15 wt.%, while at 550 and 600 °C the yield was lesser than 10 wt.%. Sanginés et al. [20] performed pyrolysis of olive stone using a rotary kiln. The system operated with a rotation speed of 3 rpm, inert gas flow rate of 200 mL/min, heating rate of 10 °C/min and final temperature of 900 °C. The maximum bio-oil yield was observed at 500 °C (37 wt.%), while the yields at 400 and 700 °C were 28 and 35 wt.%, respectively.

De Conto et al. [21], conducting pyrolysis experiments with elephant grass (*Pennisetum purpureum* S.) in a rotary kiln, obtained maximum bio-oil yield at 700 °C and 4 rpm (52.99 wt.%). The yield decreased to 44.52 wt.% at 2 rpm and decreased further at 0 rpm (37.25 wt.%). Literature states that rotary kiln reactor tends to present higher bio-oil yield when compared to other reactor types [14,15].

No study was found in literature about fodder radish pyrolysis, neither its cake (FRSC). Given the potential of fodder radish to produce biofuels (biodiesel), and consequently the generation of a waste (FRSC), the contribution of this study is to evaluate performance of a rotary kiln reactor for bio-oil production through FRSC pyrolysis. Different operational parameters (reactor rotation speed/inert gas flow rate/presence of residual oil in the biomass) were investigated and the obtained bio-oils were characterized under these conditions.

2. Materials and methods

2.1. Biomass obtainment

University of Caxias do Sul Agronomy Course provided the FRSC. Fodder radish was cultivated in a rural unit (geographical coordinates: