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A two-dimensional pyrolysis process to concentrate nicotine during tobacco leaf bio-oil production

Mohammad M. Hossain[a,b], Ian M. Scott[b,*], Franco Berruti[a], Cedric Briens[a]

[a] Institute for Chemicals and Fuels from Alternative Resources (ICFAR), Department of Chemical and Biochemical Engineering, Faculty of Engineering, Western University, London, Ontario N6A 5B9, Canada

[b] Agriculture and Agri-Food Canada (AAFC), 1391 Sandford Street, London, Ontario N5V 4T3, Canada

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ABSTRACT

Pyrolysis is a simple, inexpensive and arguably safer method to recover high-value products from plants relative to solvent extraction processes. In order to optimize pyrolysis conditions to improve the separation of selected compounds, a novel reactor-condenser chain process was developed to isolate nicotine from tobacco leaf. Ground tobacco (*Nicotiana tabacum*) leaf (< 1 mm) was pyrolyzed at 10 °C/min from ambient to 275 °C using a two-dimensional (2-D) mechanically fluidized reactor (MFR). The gases formed in the reactor would either condense in the hot (180, 190, 200 or 240 °C) or the cold (4 °C) condenser based on the boiling point of the chemicals in the vapors produced. The 2-D MFR operating conditions were optimized by a two-step process: (1) vapors were generated between ambient to 275 °C and the hot condenser temperature was varied to determine which yielded the highest nicotine concentration and recovery; and (2) the hot condenser temperature was kept constant while the best reactor temperature cut was determined. Nicotine recovery was optimal with a condenser temperature of 190 °C. A 25% nicotine concentration in the bio-oil was obtained with a nicotine recovery of 92% as the reactor temperature was increased from ambient to 275 °C. Narrowing the reactor temperature range between 260 and 275 °C maximized the nicotine concentration, as the bio-oil had a 56% nicotine concentration, with a nicotine recovery of 21%. The 2-D pyrolysis process represents a significant improvement over solvent extraction and is potentially applicable for valuable chemical recovery from biomass.

1. Introduction

Agricultural waste is an important source of bio-fuel (Vamvuka et al., 2014; Rizzo et al., 2013; Imran et al., 2014), chemical feedstock (de Wild et al., 2012; Nocquet et al., 2014) and a source of many valuable bioactive compounds (Santana-Méridas et al., 2012). Tobacco (*Nicotiana tabacum*) is an example of a high value crop that generates under-utilized residues. Tobacco plants are grown in more than 124 countries and approximately 3.8 million hectares of agricultural land is used for tobacco plant cultivation (Barla and Kumar, 2016). A huge amount of tobacco waste is generated every year during the manufacture of cigarettes which creates environmental pollution due to the release of toxic compounds including nicotine (Hu et al., 2015). Waste tobacco leaves and stems are economically important because of the potential to recover bioactive compounds, including nicotine, for other applications (Wang et al., 2008). For example, tobacco waste from the cigarette industry can be pyrolyzed to recover nicotine from leaves where the content ranged from 1.21 to 2.19% (Lee et al., 2007). An alkaloid, nicotyrine, can be produced in place of nicotine when tobacco is pyrolyzed (Ye et al., 2016). When β-nicotyrine produced during cigarette smoking has been shown to inhibit the human cytochrome P-450 2A6 (CYP2A6), the primary enzyme responsible for the oxidation of nicotine (Denton et al., 2004). There is a potential for applying this compound as part of a smoking cessation strategy (Sellers et al., 2003).

Compared to the other compounds identified after tobacco pyrolysis nicotine may have the greatest pharmaceutical application. For instance, nicotine has been found to reduce the symptoms of autoimmune (Gao et al., 2015) and Parkinson's disease (Quik et al., 2008), and improved memory recognition (Froeliger et al., 2009). A metabolite produced by *Arthrobacter nicotinovorans* degradation of nicotine, 6-Hydroxy-l-nicotine (6HLN), can improve memory formation and decrease oxidative stress in rats, suggesting that 6HLN could represent a viable therapeutic alternative to improve memory function (Hritcu et al., 2015).

Currently organic solvents are primarily used for the separation of nicotine from tobacco (Hu et al., 2015; Guo et al., 2010), but the

* Corresponding author.
E-mail address: ian.scott@agr.gc.ca (I.M. Scott).

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solvents used are expensive, hazardous and the process to purify the target compounds is time consuming (Hossain et al., 2015b). In addition, the pre-treatment of the biomass is an extra step for better separation of the target compounds through solvent extraction (Mäki-Arvela et al., 2014). A novel approach is to separate nicotine through thermochemical means, such as pyrolysis, in place of solvent extraction. A recent contribution to pyrolysis technology was the development of a mechanically fluidized reactor (MFR) that increased the recovery of nicotine from tobacco leaves (Hossain et al., 2015a). A major issue with the process, however, is that the liquid bio-oil produced by this reactor has a nicotine concentration of only 2%, although the study found the nicotine recovery was 5% more than for solvent extraction. When the bio-oil collected from MFR was dried at 50 °C, the nicotine concentration could be increased to 11%, but the nicotine recovery decreased (80%) (Hossain et al., 2015a). It was speculated that some of the nicotine evaporated or degraded when the bio-oil was heated, therefore by removing the water from the bio-oil without heating loss, the nicotine concentration can be increased at no expense to the recovery. However, since bio-oil at 100 °C or more is highly unstable and rapidly reacts to produce a solid residue (Bridgwater, 2003), one possible solution was to use a series of high and low temperature condensers following the pyrolysis reactor to separate the water from the bio-oil (Westerhof et al., 2011; Pollard et al., 2012). One of the first attempts was a fractional condensation system developed for the vapors produced from a bubbling bed reactor (Gooty, 2012; Gooty et al., 2014). The system successfully produced a nearly water-free (< 1 wt%) bio-oil in the first two condensers.

The objectives of this study were: (1) to develop MFR pyrolysis-condenser process to extract and purify nicotine from tobacco biomass and (2) to optimize the pyrolysis reactor temperature cuts and condenser temperatures to maximize the nicotine recovery.

2. Materials and methods

2.1. Plants

Tobacco plants were grown at the Agriculture and Agri-Food Canada (AAFC) research station, Delhi, Ontario, Canada. Tobacco leaves were dried at 60 °C and were then ground to pass through a 1 mm screen using a Thomas Model 4 Wiley Mill® (Thomas Scientific, Swedesboro, NJ, USA). Nicotine concentration in the dried tobacco leaf was 1.1% (Hossain et al., 2015a). Other studies determined a heating value of 12.3 MJ/kg (Cardoso and Ataíde, 2013) and the proximate and elemental composition of tobacco waste (Ye et al., 2016) (see Table 1).

2.2. Chemicals

Chemicals purchased for the study included: Dichloromethane (DCM) (99.7%), high performance liquid chromatography (HPLC) quality (Caledon Laboratories Ltd., Georgetown, Ontario, Canada), sodium hydroxide (NaOH) (97%) and (-)-nicotine (98.7%), reagent grade and analytical grade (Sigma-Aldrich, Oakville, Ontario, Canada), respectively.

Table 1
Proximate and elemental composition analysis of tobacco (dry basis, wt%). Modified from Ye et al. (2016).

Proximate composition	(wt%)
Volatile	63.83
Ash	18.94
Fixed carbon	17.23
Elemental composition	**(wt%)**
C	42.48
H	6.09
N	1.92
S	1.08

2.3. Tobacco leaf pyrolysis

Differences in tobacco leaf particle size between 0.212 and 1 mm were previously determined to have no significant effect when heated at 10 °C/min in terms of nicotine recovery from the biomass (Hossain et al., 2015a). It was also determined that most of the nicotine was released below 275 °C. Therefore, the present study used < 1 mm particle size dried tobacco leaf and focused on the reactor temperature range between ambient and 275 °C, with a 10 °C/min reactor heating rate.

The MFR (Fig. 3.1 in Hossain, 2016) was located at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR), Western University, London, Ontario, Canada. It is a batch reactor, thus the biomass was placed in the cylindrical reactor chamber before the experiment. The chamber is 15 cm in diameter and 25.4 cm in height, and equipped with a stirrer for better heat transfer (Fig. 1). An advantage of the MFR is that it does not require nitrogen or other inert gases to fluidize the biomass, therefore avoiding any dilution of the bio-oil vapors and, thus facilitating condensation. The MFR has two band heaters controlled by a Watlow's EZ-ZONE® PID controller (St. Louis, MO, USA). A train of two condensers in series was used. The first, hot condenser was immersed in a hot bath containing heat transfer liquid that was maintained at 180, 190, 200 or 240 °C. The gases and vapors exiting from the first condenser entered a second condenser immersed in an ice-bath (4 °C) and the non-condensable gases from the second condenser were then passed through a cotton demister and exhausted. Six different condenser trains were used. The bio-oil was collected with a different condenser train for each of six different reactor temperature cuts (ambient-180, 180–210, 210–230, 230–245, 245–260 and 260–275 °C). The reactor temperature was held for 30 min at the end for each temperature cut. The temperature of the hot bath condenser was changed for each MFR pyrolysis run and each run was completed in duplicate.

Definition of one-dimensional (1-D) and two-dimensional (2-D) MFR pyrolysis process:

When any bio-oil cut is collected only in a cold condenser from a restricted range of reactor temperatures then it is termed as a 1-D MFR pyrolysis process. When a bio-oil cut is collected from a restricted range of reactor temperatures in a train of hot and cold condensers then it is termed as a 2-D MFR pyrolysis process since the bio-oil cut is fractionated and collected at different condenser temperatures instead of being collected in a single cold condenser.

2.4. Analysis of nicotine in bio-oil

Bio-oil sample preparation and gas chromatography-flame ionization detector (GC-FID) method was described in Hossain et al. (2015a). Each temperature cut of 100 µL bio-oil was weighed, and 4 mL Milli-Q® water (EMD Millipore, Billerica, MA, USA), 2 mL 10% NaOH and 4 mL DCM were added. The sample was vortexed (1 min), sonicated (5 min), shaken (10 min) and allowed to separate (3 h). The DCM layer was filtered by a nylon membrane syringe filter (0.2 µm pore size) and 2 µL was injected into the GC-FID (Hewlett Packard 5890 Series II). The samples were compared to an authentic standard of nicotine. The GC system was equipped with a Phenomenex ZB-5HT column (30 m × 0.25 mm and film thickness 0.25 µm) (Torrance, CA, USA). The GC conditions were as follows: injector temperature 250 °C; inlet pressure 7 psi. The GC run conditions were as follows: 50 °C for 0.5 min; increase 5 °C/min to 125 °C; increase 2 °C/min–155 °C and hold for 8 min; increase 25 °C/min–260 °C and hold for 8 min. The MS detector temperature was 275 °C. The nicotine extraction and quantification method were modified from Kaldis et al. (2013) using a GC-FID and an external standard as described by Docheva et al. (2014).