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9 Investigation of *in-situ* and *ex-situ* catalytic pyrolysis of miscanthus x
10
11 giganteus using a PyGC-MS microsystem and comparison with a bench-scale
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14 spouted-bed reactor
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20 *David P. Gamliel, Shoucheng Du, George M. Bollas and Julia A. Valla**
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23 Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs
24
25

26
27 191 Auditorium Road, Unit 3222, Storrs, CT 06269-4602
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32

33
34 ***Corresponding Author**
35

36 Julia A. Valla
37

38 Department of Chemical & Biomolecular Engineering
39

40 University of Connecticut
41

42 191 Auditorium Road, Unit 3222
43

44 Storrs, CT 06269-4602
45
46

47 Email: valla@engr.uconn.edu
48
49

50 Tel: +860 4860583
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Abstract

The objective of the present work is to explore the particularities of a micro-scale experimental apparatus with regards to the study of catalytic fast pyrolysis (CFP) of biomass. *In-situ* and *ex-situ* CFP of miscanthus x giganteus were performed with ZSM-5 catalyst. Higher permanent gas yields and higher selectivity to aromatics in the bio-oil were observed from *ex-situ* CFP, but higher bio-oil yields were recorded during *in-situ* CFP. Solid yields were comparable across both configurations. The results from *in-situ* and *ex-situ* PyGC were also compared with the product yields and selectivities obtained using a bench-scale, spouted-bed reactor. The bio-oil composition and overall product distribution for the PyGC *ex-situ* configuration more closely resembled that of the spouted-bed reactor. The coke/char from *in-situ* CFP in the PyGC was very similar in nature to that obtained from the spouted-bed reactor.

Keywords

Biomass Catalytic Fast Pyrolysis (CFP), *Ex-Situ* vs. *In-Situ* CFP, Pyrolysis Gas Chromatography (PyGC), Spouted-Bed Reactor, ZSM-5 Catalyst

1. Introduction

Biomass pyrolysis provides a renewable and sustainable option for the production of liquid hydrocarbons and valuable chemicals. The resulting liquid product, bio-oil, consists of aromatic compounds, organic oxygenated species and water. Catalytic fast pyrolysis (CFP) is the pyrolysis of biomass at high heating rates, in the presence of catalyst, which enhances the bio-oil selectivity and yield to deoxygenated compounds (Carlson et al., 2011). ZSM-5 has been shown to be the best suited CFP catalyst, due to its shape selective pore structure and low affinity for coke formation (Jae et al., 2011). The catalyst to biomass (C/B) ratio, biomass heating rate and pyrolysis temperature are important variables, which must be optimized to maximize bio-oil yield and quality (Carlson et al., 2008).

Catalytic upgrading of pyrolysis vapors can be carried out either *in-situ* the pyrolysis step or *ex-situ*. *In-situ* CFP entails pyrolysis and catalytic upgrading occurring in a one-step, single reactor process. *Ex-situ* CFP requires transfer of the pyrolysis vapors from the initial pyrolysis reactor to a secondary reactor for catalytic upgrading. Wan et al. (Wan and Wang, 2014) outlined several differences between the *in-situ* and *ex-situ* CFP configurations. They recognized that effective conversion of oxygenated compounds to stable hydrocarbons is possible via either configuration. However, the vapors formed during *in-situ* CFP may not contact significant amounts of catalyst, and thus, a higher C/B ratio is required to attain the same level of deoxygenation. Additionally, the optimum pyrolysis temperature may not be ideal for upgrading, and therefore, a separate *ex-situ* reactor may facilitate upgrading under more suitable conditions. Char formed on the catalyst during *in-situ* CFP may also result in accelerated catalyst deactivation due to pore blockage. *Ex-situ* upgrading has the potential to resolve the aforementioned issues, but it requires heating two reactors.

Several recent studies have focused on a direct comparison between *in-situ* and *ex-situ* CFP. Wan and Wang, (2014) constructed an *ex-situ* reactor system for a pre-existing micropyrolyzer, and studied *in-situ* vs. *ex-situ* CFP of oak and levoglucosan. Higher aromatic yields were observed with *in-situ* CFP. They argued that vapor residence time in the catalyst pores for *in-situ* CFP is very high (>10 s), which led to very high conversions to secondary products (aromatics and coke). Nguyen et al. (2013) studied *in-situ* and *ex-situ* CFP of woodchips at a constant C/B ratio over faujisite type zeolites. They noted higher liquid deoxygenation capabilities for *ex-situ* CFP. They attributed this observation to the temperature gradient created by heating the catalyst and biomass at the same time during *in-situ* CFP, as opposed to *ex-situ* CFP, where the catalyst is typically pre-heated in the downstream unit. Güngör et al. (2012) compared pine bark pyrolysis in a “one-step” and “two-step” system, and concluded that the *ex-situ* system was the most appropriate configuration to maximize bio-oil yield and oxygen removal at high temperature. On the contrary, Yildiz et al. (2013) concluded that *in-situ* CFP is more attractive, because they observed about double the yield to aromatics. However, more catalyst was required to attain high quality bio-oil during *in-situ* CFP. Wang et al., (2014a) studied *in-situ* and *ex-situ* CFP of poplar at very high C/B ratio and temperature (20:1 and 700 °C, respectively) in a tandem microreactor system. They found significantly higher yields to permanent gas and olefins accompanied by lower yields to aromatic hydrocarbons using *ex-situ* CFP. They also observed significantly increased coke and char buildup when performing *in-situ* CFP. The aforementioned studies provide insight into the differences between *in-situ* and *ex-situ* CFP. However, a direct comparison of the *in-situ* and *ex-situ* CFP with an investigation of the effects of varying C/B ratio on the product distribution has not been published yet.

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5 Pyrolysis gas chromatography (PyGC) offers an attractive microscale technique for
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8 studying biomass pyrolysis. Small amounts of biomass and catalyst are required, and ease
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10 of operation makes PyGC a widely applied laboratory tool for rapid screening of various
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12 biomass types and catalysts (Srinivasan et al., 2012). PyGC offers excellent control of
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14 process conditions including temperature, pressure, C/B ratio and heating rate. However,
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16 these systems have several drawbacks including inefficient mixing of catalyst and biomass
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18 and inability to be scaled up to a continuous industrial process (Carlson et al., 2011).
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23 Several bench and pilot scale reactor types have been developed to study biomass CFP in
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25 a more industrially realistic environment. Fixed bed reactors have been used for CFP, but
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27 slow heat transfer rates result in limited bio-oil and high char yields (Bridgwater, 2003).
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29 Fluidized bed reactors have been widely studied and applied due to their scaling ability,
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31 continuous operation capability, and ease of mixing and heat transfer (Bollas et al., 2003;
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33 Mante et al., 2014). The spouted-bed reactor is a type of fluidized bed reactor, which is
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35 adept at handling large particles and particle size distributions, provides excellent mixing
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37 and can handle different feedstocks (Cui and Grace, 2008). Olazar et al. (2000) studied
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39 biomass CFP in a spouted-bed and concluded that the utilization of the catalyst *in-situ*
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41 provides excellent gas-solid contact, and that pyrolysis and upgrading temperatures of 500
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43 °C are optimal. Du et al. (2014) illustrated the design of a spouted-bed reactor, and
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45 investigated the ideal operating conditions for the CFP of miscanthus x giganteus.
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52 In summary, a PyGC provides fast screening of various biomass types and catalysts, in
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54 either the *in-situ* or *ex-situ* configuration. However, which of these configurations more
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56 closely resembles the operation of realistic, laboratory-scale reactors has not been
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58 determined yet. Limited information on the comparison between the microscale PyGC
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5 system and the bench-scale reactors is available in the literature. The primary objective of
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7 this study is to directly compare *in-situ* and *ex-situ* CFP in a PyGC system. A wide range of
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9 C/B ratios are used for both configurations to provide insight with regards to primary and
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11 secondary product formation and operational dynamics in each configuration. The *in-situ*
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13 and *ex-situ* PyGC experimental results are compared with the results obtained from a
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15 bench-scale, spouted-bed reactor operated under identical conditions. The objective of the
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17 aforementioned study is to provide guidance with respect to the applicability and suitability
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19 of each configuration in predicting the performance of a bench-scale system. These results
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21 will allow us to establish a refined method for operation of the PyGC system to accurately
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23 screen catalyst functionality, operating conditions and biomass feedstocks.
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32 **2. Methods**

33 **2.1 Feedstock and Catalyst**

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35 Miscanthus x giganteus was the biomass of choice, and commercial spray dried ZSM-5
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37 catalyst from W.R. Grace & Co. was used as the catalyst. Properties and preparation of the
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39 biomass (including ultimate and proximate analysis) and the catalyst can be found in our
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41 recent study (Du et al., 2014).
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50 **2.2 Pyroprobe Apparatus**

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52 Pyrolysis experiments were performed using a PyGC system (CDS Analytical Inc.
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54 5200HP). A simplified schematic of the reaction system is shown in the Supplemental
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56 Information. The pyrolysis reaction takes place in a quartz tube microreactor (1.9 mm I.D.,
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58 25 mm length), surrounded by a resistively heated coil probe. Catalytic upgrading reactions
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5 take place either in the pyrolysis microreactor (*in-situ* CFP) or a tandem fixed bed reactor
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7 (*ex-situ* CFP). The downstream fixed bed reactor is a removable stainless steel tube (3.5
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9 mm I.D., 85 mm useable length) housed in an external furnace.
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12 13 14 15 **2.3 Experimental Procedure**

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17 PyGC experiments were performed in either the *in-situ* or *ex-situ* CFP configuration
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19 using methods very similar to those found in literature (Carlson et al., 2011; Srinivasan et
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21 al., 2012; Thangalazhy-Gopakumar et al., 2012). Biomass and catalyst were mixed together
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23 prior to *in-situ* experiments, and 5 mg of biomass and catalyst mixture was inserted into the
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25 quartz tube microreactor. When in the *ex-situ* configuration, the microreactor was loaded
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27 with 2 mg of biomass, while the catalyst (2 - 20 mg) was packed in the tandem fixed-bed.
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32 The pyrolysis microreactor housing, or interface, was maintained at 300 °C for the
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34 duration of the pyrolysis step to prevent condensation of product vapors. The coil around
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36 the microreactor was heated to the desired pyrolysis temperature and maintained
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38 isothermally for 20 seconds. Every experiment in the present work was performed at a
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40 pyrolysis and upgrading temperature of 600 °C. Condensable vapors were adsorbed onto a
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42 cold trap (Tenax, Dow Chemical) and non-condensable gas was directed to an online MS
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44 (Agilent 5975C), calibrated for H₂, CO, CO₂, CH₄, C₃H₆ and Ar. After the reaction process,
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46 the condensable products were desorbed from the trap and transferred through a heated line
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48 to a GC equipped with an MS detector (Agilent 6890 GC with 5973N MS). The GC
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50 column was an Agilent DB-5 (0.32 µm ID, 30 m length). The GC-MS was calibrated by
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52 injecting external standards through the PyGC system. Over 350 total individual
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5 compounds were detected by the GC-MS, but only those with a qualifier greater than 75
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7 were quantified.
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10 Solid yield was determined by oxidizing the remaining organic residue at 800 °C, while
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12 monitoring the CO and CO₂ response on the MS. Temperature programmed oxidation
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14 (TPO) of solid residues from each configuration was performed with a thermogravimetric
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16 analyzer (TGA, TA Instruments Q-500). ZSM-5 zeolite (Zeolyst International, CBV8014)
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18 was used to better show the effects of C/B ratio on char formation.
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22 Preliminary experiments indicated that a reaction time of 20 s at 600 °C was enough to
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24 pyrolyze all volatile biomass in the microreactor. Similar results were found by Carlson et
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26 al., (2010) for glucose pyrolysis in a comparable PyGC system. Microreactor loading was
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28 also found to have a significant effect on product yields, indicating mass transfer limitations
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30 in the system. A constant loading was maintained to ensure uniform experimental
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32 conditions. Only experiments with a carbon balance of 100% +/- 15% were accepted, and
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34 all experiments were performed in triplicate to ensure precision.
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39 Laboratory scale CFP of miscanthus has been performed using a specially designed
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41 spouted-bed reactor. The experimental conditions and procedure for the spouted-bed
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43 reactor have been reported by Du et al., (2014). The pyrolysis temperature, ZSM-5 catalyst,
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45 and the C/B ratio in the spouted-bed and the Py-GC experiments were the same. A
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49 summary of the experimental conditions for all configurations can be found in Table 1.
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3. Results and Discussion

3.1 *In-situ* vs *Ex-situ* Catalytic Fast Pyrolysis in PyGC

3.1.1 *In-situ* CFP

In-situ CFP was performed by mixing ZSM-5 catalyst and miscanthus prior to pyrolysis. C/B ratios of 1, 2, 5 and 10 were tested. The results of the CFP experiments are presented in Figure 1. Figure 1(A) shows the overall carbon balance, and the carbon yields to solids, liquids and permanent gas. The solid carbon yields slightly increased up to a maximum of 60% at low C/B ratios, and decreased at higher C/B ratio. Permanent gas carbon yield increased as a function of C/B ratio, up to 21%. Finally, the liquid carbon yield also increased with C/B ratio to a final value of approximately 20%.

A detailed permanent gas analysis is presented in Figure 1(B). The overall gas carbon yield increased with C/B ratio, mainly driven by a rise in the CO carbon yield, which increased from 5% to 13%. The CO₂ carbon was almost constant as a function of C/B ratio. Very small amounts of methane were detected, and the carbon yield to methane remained approximately constant at 2%. No propylene was detected in any of the *in-situ* CFP experiments.

The composition of the liquid bio-oil product is presented in Figure 1(C). At low C/B ratio, oxygenated species, such as phenols, furans and other oxygenates dominated the liquid products. The phenols group in Figure 1(C) includes phenol, methyl phenols, and polyols. The furans group primarily includes furfural, furan, fuanones and benzofurans. Many other oxygenates were detected as part of this analysis, including guiacols, carboxylic acids, pyrans, ketones and aldehydes, most of which were substituted aromatics. As C/B ratio is increased, the carbon yield to mono-aromatic hydrocarbons, including

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5 benzene, toluene, xylene, styrene and alkyl benzenes (e.g. ethyl benzene) and poly-aromatic
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7 hydrocarbons (PAHs) including naphthalenes and indenenes increased. The naphthalenes
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9 group consists primarily of naphthalene, methyl naphthalenes, dimethyl naphthalenes and
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11 alkyl naphthalenes. The indenenes category includes indene, methyl indene and alkyl indenenes.
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13 Other PAHs include phenanthrenes, anthracenes and pyrenes. At high C/B ratio, the liquid
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15 products consisted of mostly aromatic hydrocarbons, with oxygenated species only making
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17 up a small portion of the liquid products. The high initial liquid carbon yield was a result of
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19 the high selectivity to oxygenated compounds, which decreased as a function of C/B ratio.
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21 The 1:1 liquid product distribution closely resembles that obtained from the fast thermal
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23 pyrolysis of miscanthus, performed as a part of this study. The thermal pyrolysis results are
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25 presented in the Supplemental Information.
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32 **3.1.2 *Ex-situ* CFP**

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34 Fast pyrolysis was performed in the quartz microreactor followed by *ex-situ* vapor
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36 upgrading in the tandem fixed-bed reactor. In each experiment, the quartz microreactor was
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38 loaded with biomass, and the downstream reactor was packed with catalyst. Biomass was
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40 pyrolyzed under the same conditions as the *in-situ* CFP configuration, and the pyrolysis
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42 vapors were transferred to the tandem fixed-bed reactor maintained at 600 °C.
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47 Figure 2(A) presents the liquid, solid and gas carbon yields as a function of C/B ratio.
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49 The liquid carbon yield increased with C/B ratio, from 4% to 12%. Permanent gas carbon
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51 yield slightly increased from 30% to 34% over the C/B ratios tested. The solid carbon yield
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53 decreased from 62% to 54%. The results of the gas analysis are presented in Figure 2(B).
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55 The overall gas carbon yield increased with increasing C/B ratio. As in the case of *in-situ*
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57 CFP, this increase is mainly a result of the increase in CO yield with C/B ratio. The CO₂
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yield increased very slightly to a maximum of 17%, and the methane yield slightly decreased as a function of C/B ratio. Very small (<0.5%) amounts of olefins were sporadically detected, and were not quantified in this study.

The liquid product analysis is presented in Figure 2(C). Aromatic compounds were present in significant yields over the range studied. At low C/B ratio, the liquid product was a mix of both aromatics and oxygenated compounds, phenolic compounds being the dominant oxygenates. As C/B ratio increased, the carbon yields to aromatic compounds increased significantly. At a 10:1 C/B ratio, aromatic carbon selectivity was close to 80%.

3.1.3 Comparison between *in-situ* and *ex-situ* CFP

The experimental results from *in-situ* and *ex-situ* CFP in the PyGC highlight several inherent differences between each configuration. The overall solid carbon yields remained essentially the same across the two configurations. The primary differences between the two configurations were observed in the liquid and permanent gas carbon yields and product distribution. *In-situ* CFP resulted in significantly higher liquid carbon yields and a lower overall permanent gas carbon yield, whereas *ex-situ* CFP resulted in considerably higher permanent gas carbon yields, and lower liquid carbon yields. The effect of C/B ratio is essentially the same for both configurations, namely an increase in the carbon yield to aromatic compounds as a result of the deoxygenation of liquid oxygenates. One significant difference between the two configurations is the selectivity to different compounds. Naphthalenes and oxygenates were much more dominant during *in-situ* CFP, whereas mono-aromatic hydrocarbons were slightly favored during *ex-situ* CFP. This is consistent with Nguyen et al. (2013) who found a higher degree of deoxygenation during *ex-situ* CFP.

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5 They suggested that the different solid particle size scales and heat transfer limitations in
6 the *in-situ* configuration **may** result in more oxygenated products.
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10 Wang et al. (2014a) studied *in-situ* and *ex-situ* CFP of poplar wood over ZSM-5 zeolite
11 in a similar microreactor system, and found the same increase in permanent gas products
12 with *ex-situ* CFP. However, the composition of the permanent vapors consisted mainly of
13 olefins. Additionally, they observed significantly higher solid residue yields for *in-situ* CFP
14 compared to *ex-situ* CFP. These differences may be attributed to the relatively high C/B
15 ratio, catalyst and reaction temperature (20 C/B, ZSM-5 zeolite, 700 °C) in their study.
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17 They also suggested that higher temperature favors the production of olefins, while lower
18 temperatures favor the production of aromatic species.
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30 Few studies have been conducted that directly compare *in-situ* and *ex-situ* CFP in one
31 reaction system. Some studies compare *in-situ* CFP in a microreactor system with fast
32 pyrolysis in a laboratory scale reactor followed by *ex-situ* fixed-bed upgrading (Carlson et
33 al., 2011, 2009; Compton et al., 2011). Compton et al. (2011) found higher liquid yields for
34 oak pyrolysis using an *in-situ* microreactor method in comparison to fast pyrolysis followed
35 by upgrading in an external *ex-situ* fixed-bed reactor, which is consistent with the results in
36 the present study. Carlson et al. (2011) pyrolyzed furan, a biomass model compound, in
37 both a PyGC and fixed-bed reactor. They found that coke and aromatic yields are higher
38 with the *in-situ* CFP method compared to *ex-situ* fixed-bed pyrolysis. There are three
39 possible explanations for higher bio-oil yields during *in-situ* CFP: 1) the heating rate of the
40 bulk C/B mixture may be significantly slower than that of the heating coils during *in-situ*
41 CFP, compared to *ex-situ* CFP, where the catalyst is pre-heated in the tandem fixed bed; 2)
42 more rapid catalyst deactivation during *in-situ* CFP, due to char buildup on the surface of
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the catalyst (Valle et al., 2007), resulting in higher yields to intermediate oxygenated liquid products; and 3) higher residence/catalyst-contact times of biomass pyrolysis vapors during *in-situ* CFP, relative to the residence time of pyrolysis vapors in the *ex-situ* upgrading reactor; in the former case, biomass is intimately mixed and must diffuse through the catalyst to exit the pyrolysis microreactor (Carlson et al., 2011).

Figure 3 depicts the carbon yield and carbon selectivity to aromatic products for the *in-situ* and *ex-situ* CFP configurations. Selectivity is defined as the carbon yield to aromatic products divided by the lumped carbon yield to liquid products. Aromatic compounds include benzene, toluene, xylenes, alkyl-benzenes, naphthalenes and other PAHs. At low C/B ratios the carbon yield to aromatic compounds was approximately the same for both *in-situ* and *ex-situ* CFP. As the C/B ratio increased, *in-situ* CFP resulted in a higher amount of biomass converted to aromatic compounds compared to *ex-situ* CFP. On the other hand, *ex-situ* CFP resulted in higher carbon selectivity to aromatic compounds at all C/B ratios. However, the gap in aromatic selectivity between *ex-situ* and *in-situ* CFP diminished significantly as the C/B ratio increased. In summary, at low C/B ratios both *in-situ* and *ex-situ* CFP resulted in low carbon aromatic yields; the advantage of *ex-situ* CFP is the higher carbon selectivity to aromatics. When the C/B ratio increases significantly, both *in-situ* and *ex-situ* CFP resulted in bio-oil with the same, very high carbon selectivity to aromatics; the advantage of *in-situ* CFP is the high biomass carbon conversion to liquid aromatics. To the best of our knowledge, this is the first time the effect of C/B ratio on aromatic yield and selectivity has been directly compared for *in-situ* and *ex-situ* CFP.

3.2 Comparison of *in-situ* and *ex-situ* CFP in PyGC to Spouted-bed Reactor

One of the primary goals of this study is to understand if pyrolysis in the microscale PyGC can accurately predict the effects of operating conditions and determine the pyrolysis product distribution obtained from a more realistic bench-scale reactor system. For this reason, the miscanthus *in-situ* and *ex-situ* PyGC experimental results obtained in this study are compared with the corresponding results of miscanthus CFP performed in a spouted-bed reactor. The results of the latter study were presented in detail by Du et al., (2014).

Figure 4 is a comparison of the lumped product yields obtained from the *in-situ* (A) and *ex-situ* (B) PyGC configurations and CFP in the spouted-bed reactor (C). Water is not taken into consideration, as it is difficult to account for in the PyGC experiments. The trends of increasing C/B ratio in PyGC experiments are much less pronounced than for the spouted-bed reactor experiments. The bio-oil yield obtained from both the spouted-bed reactor and *ex-situ* PyGC experiments increase as a function of C/B ratio. The permanent gas yield followed the same trend in all three configurations; however, the permanent gas yield from *ex-situ* CFP was higher at lower C/B ratios than from *in-situ* CFP and the spouted-bed reactor. Finally, the solid yield remained approximately constant with C/B ratio for *in-situ* CFP, whereas it decreased for *ex-situ* CFP and the spouted-bed reactor.

A comparison of the liquid product distribution from the three reactor configurations may be found in the Supplemental Information. The liquid product distributions from the spouted-bed and *ex-situ* CFP of miscanthus were very similar. Both consisted mainly of aromatic hydrocarbons, while oxygenates in the form of phenols and furans were limited. This is a significant difference compared to the bio-oil produced from *in-situ* CFP, which had significantly more oxygenates. Furthermore, in all configurations, all aromatic

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5 compound yields increased as a function of C/B ratio. The liquid selectivity to aromatics is
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7 much higher in the spouted-bed reactor, almost 96% at 600 °C (C/B=5), whereas the
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9 maximum aromatic liquid selectivity observed from the PyGC experiments was
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11 approximately 80% (*ex-situ*, C/B=10). The only difference in the composition of the bio-oil
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13 produced by *ex-situ* CFP in the PyGC compared to the spouted-bed, was the increased
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15 presence of naphthalenes and higher order PAHs, relative to mono-aromatic hydrocarbons.
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17 This may be attributed to the larger residence time and quality of mixing in the spouted-
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19 bed, resulting in higher extent of catalytic reactions, and consequently, in more PAHs
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21 (Carlson et al., 2010). A more detailed discussion of the reaction mechanism follows in
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23 Section 3.3.
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30 An analysis of the permanent gas product distribution from each configuration reveals
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32 significant differences (Figure S4 in Supplementary Information). First, substantial
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34 amounts of olefins were present in the spouted-bed permanent gas products, whereas
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36 almost no olefins were observed in either PyGC configuration (*in-situ* or *ex-situ*). There is
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38 also a discord in the ultimate yields of CO and CO₂. Both CO and CO₂ yields increased as a
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40 function of C/B ratio for *in-situ* and *ex-situ* CFP. More CO₂ was produced from both *in-situ*
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42 and *ex-situ* CFP in the PyGC than the spouted-bed, whereas more CO was formed from
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44 CFP in the spouted-bed. The ultimate yield of CO and CO₂ is feedstock dependent (Zhang
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46 et al., 2007). However, in this case the feedstock is the exact same, so that is not a factor.
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48 This indicates that decarbonylation and decarboxylation are a result of catalytic activity,
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50 while process conditions affect these reaction pathways.
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57 The gas analysis results are very consistent with Carlson et al. (2011) who observed
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59 lower CO yields and no olefinic products, when performing CFP of pine in a PyGC
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5 compared to a fluidized bed reactor. The exact same phenomenon was also reported by
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7 Patwardhan et al. (2011) when comparing cellulose pyrolysis in a PyGC to fluidized bed
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9 pyrolysis. An acid catalyst would deoxygenate furans, phenols and other oxygenates to
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11 form aromatics, water, CO or CO₂ and coke at 600 °C. Oxygenates in the bio-oil generated
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13 during *in-situ* CFP in the PyGC, which are mostly phenols, simply have not reacted to form
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15 CO, so CO₂ becomes the dominant product. The absence of olefins can be explained along
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17 the same lines; olefins are a product of catalytic decomposition of oxygenates at high
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19 temperature (Cheng and Huber, 2011). The intimate contact between biomass and
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21 preheated catalyst is much better in the spouted-bed, resulting in a higher extent of reaction
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23 and the consistent formation of olefins.
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30 It has been reported that coke and char formation are greater in the PyGC than in bench
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32 scale units (Torri et al., 2010). In this study, higher coke and char yields in the PyGC were
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34 only observed at high C/B ratio. At low C/B ratio, less coke and char was formed in PyGC
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36 CFP than in the spouted-bed. In the literature this phenomenon is attributed to higher
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38 residence time in the *in-situ* microreactor and slower heat transfer rates resulting in
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40 increased coke and char formation (Torri et al., 2010). At higher C/B ratio, the pyrolysis
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42 products must diffuse through the catalyst, resulting in increased coke formation and a
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44 higher overall solid yield.
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52 **3.3 Formation of Primary and Secondary Pyrolysis Products**

53 **3.3.1 Composition of Liquid and Permanent Gas Products**

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55 CFP mechanisms have been a focal point in the literature, especially with regards to the
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57 production of aromatics, olefins and coke (Cheng and Huber, 2012; Mettler et al., 2014;
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Vinu and Broadbelt, 2012; Wang et al., 2014a). Mettler et al. (2012a) described and elaborated on their previously proposed pyrolysis mechanism using a novel thin film pyrolysis microreactor technique. They found that the primary products of cellulose pyrolysis include furfurals, furans, glucopyranoses and pyrans. Patwardhan et al. (2011) have also studied primary and secondary reactions of cellulose pyrolysis. They concluded that the micropyrolyzer may limit the extent of secondary pyrolysis reactions. Primary reactions were defined as reactions that occur within the first 15-20 ms of pyrolysis and produce mainly furans, furfurals and soluble sugars (levoglucosan). Wang et al. (2014b) pyrolyzed cellulose, hemicellulose and lignin separately in a micropyrolyzer system, and grouped primary pyrolysis products into three categories based on the origin of each species. Their results indicate that soluble sugars, carboxylic acids and furans are a result of cellulose and hemicellulose decomposition, whereas phenols and guaicolols are a result of lignin pyrolysis. Primary product formation and absence of catalytic activity, could explain the high amount of liquid products for the *in-situ* CFP experiments observed at low C/B ratio. Under these conditions, the biomass was thermally pyrolyzed and the vapors travelled away from the microreactor before coming into contact with hot catalyst. At higher C/B ratio, the vapors are forced to diffuse through the catalyst prior to exiting the pyrolysis microreactor.

Figure 5 shows the correlations between CO yield and lumped aromatic and oxygenate yield from *in-situ* CFP, *ex-situ* CFP and CFP in the spouted-bed reactor. Aromatic yield clearly increased with increasing CO yield, and the corollary decrease in oxygenate yield was observed. The trend between aromatic and CO yield for the spouted-bed was initially proposed to be linear (Foster et al., 2012). However, the results from the present study

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5 indicate that this trend may be exponential in the regime the PyGC was operated at. The
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7 same trends were observed for both the *in-situ* and *ex-situ* PyGC configurations. This trend
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9 mostly mirrors the decrease in phenols as a function of C/B ratio. The relationship between
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11 CO₂ and the liquid product distribution is slightly more complicated. Little CO₂ and many
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13 other oxygenates are formed at low C/B ratio, whereas the opposite is true at high C/B
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15 ratios. The other oxygenates category consists mainly of ketones and carboxylic acids, so it
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17 is fair to claim that those compounds are more likely to undergo decarboxylation than
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19 decarbonylation. There is no apparent trend between CO₂ and the liquid products for the *ex-*
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21 *situ* case, as there are very few other oxygenates. The very high CO₂ yields come at the
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23 expense of valuable liquid products. It has been proposed that CO₂ production is more
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25 favorable than CO, because it makes the most efficient use of 1 carbon atom to bind 2
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27 oxygen atoms, resulting in the most deoxygenated liquid product possible (Wang et al.,
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29 2014b). However, deoxygenation of the bio-oil clearly comes at the expense of overall
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31 liquid yield.

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33 A CFP mechanism (shown in the Supplemental Information) is proposed from these
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35 results, with input from several other sources (Cheng and Huber, 2012; Mettler et al.,
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37 2012a; Saidi et al., 2014). All products proposed in the mechanism were detected as part of
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39 our analysis, and are meant to be representative, though not inclusive, of the pyrolysis
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41 products. The three initial components of biomass (cellulose, hemi-cellulose and lignin)
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43 break down in a thermal reaction to form primary pyrolysis products, namely soluble
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45 sugars. These sugars further thermally decompose to form carboxylic acids. These
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47 carboxylic acids may then undergo a series of dehydration, decarboxylation, fragmentation,
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49 condensation and cyclization reactions to form functionalized furans (Vinu and Broadbelt,
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2012). Lignin may also break down to form guaicol, which further react to form phenols. Char is also considered a primary product, although the presence of catalyst *in-situ* transforms its structure (*vide infra*). These primary products then react over the ZSM-5 catalyst to form aromatics, olefins, and finally coke. The pyrolysis operating conditions, such as the temperature, the C/B ratio and the residence time, as well as the *in-situ* or *ex-situ* configuration determines the extent of each reaction pathway.

3.3.2 Coke and Char Formation

Char is defined as any organic solids remaining as a byproduct of thermal pyrolysis. Coke is defined as carbonaceous deposits in the catalyst pores resulting in deactivation. S. Du et al. (2013) have investigated in detail the origins and the mechanisms of formation of char and coke and have demonstrated that char is oxygen rich, while coke is oxygen deficient in structure. In the present study, for the *ex-situ* CFP configuration, the char yield represents what remains in the microreactor after thermal pyrolysis, and the coke yield represents the coke deposited in the tandem reactor. The formation of coke causes a loss of catalytic activity during both *in-situ* and *ex-situ* CFP (Cheng and Huber, 2011; Valle et al., 2007). Additionally, catalyst performance may suffer from surface coverage and blockage due to the buildup of char (Elordi et al., 2011). As a result, the separation of thermal pyrolysis and catalytic upgrading (*ex-situ*) may have a benefit, as the catalyst does not lose accessibility due to external char formation.

A comparison of the characteristics of coke and char was investigated by performing TPO and is presented in Figure 6(A). The area under the curve is proportional to the coke/char fraction in each configuration, but the peak areas are not comparable across experiments due to the different solid yields. The differential thermogram (dTG) of the

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5 char/coke obtained from *in-situ* CFP experiment had one large char peak at 500 °C, and a
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7 smaller coke peak at 610 °C. There are two curves for the *ex-situ* configuration, one from
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9 the char remaining in the pyrolysis microreactor, and the other from coke deposited on the
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11 catalyst in the tandem fixed-bed reactor. The dTG of the char from the pyrolysis
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13 microreactor exhibited a single peak at 425 °C, with a shoulder at 325 °C. The coke
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15 deposited in the catalyst had a single broad peak with a maximum at 670 °C. The char/coke
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17 formed in the spouted-bed mimicked the bimodal distribution obtained by *in-situ* CFP, with
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19 a large char peak at 485 °C and smaller coke peak at higher temperature (620 °C). These
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21 results indicate that the structure of char from the CFP method is different than that of
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23 thermal pyrolysis, indicating that the catalyst has an effect on the structure of thermal char.
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25 Mettler et al. (2014) proposed a reaction scheme for catalytic cellulose pyrolysis, where
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27 different precursors of char, termed primary and secondary, are proposed. In their scheme,
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29 the secondary char is a result of the secondary pyrolysis of furanic compounds. Coke and
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31 char have also been investigated in our previous work (Du et al., 2013), and we proposed
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33 that primary char is a result of condensed aggregated sugars. We believe that the difference
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35 in the char structure between *in-situ* and *ex-situ* CFP is a result of the interaction between
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37 the catalyst and liquid oxygenates, given the high yields of furans and oxygenates detected
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39 in the *in-situ* configuration. Figure 6(B) shows the effect of C/B ratio on char formation for
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41 an unsupported ZSM-5 zeolite. The unsupported zeolite has higher activity than the
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43 supported zeolite, so this experiment is a better demonstration of the catalytic effect on char
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45 formation. The area under the char peak decreased significantly, and the peak temperature
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47 shifted to the right, as a function of C/B ratio. This indicates that despite the fact that both
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49 the char and catalyst are in a theoretically immobile solid phase, the formation of char is
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5 heavily dependent on the presence of the catalyst due to the availability of different
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7 precursors. Conversely, char may cause significant catalyst deactivation as a result of this
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9 interaction.
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12 It was also observed from the area under the dTG curves that the fraction of coke on
13 catalyst is significantly reduced during *ex-situ* CFP, compared to *in-situ* CFP. This could be
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15 a result of the theoretical increased catalyst to feed ratio for *ex-situ* CFP. The feed to the
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17 tandem *ex-situ* reactor consists of volatile bio-oil and permanent gas, whereas biomass is
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19 the feed for *in-situ* CFP. Therefore, there is less buildup of coke, relative to the amount of
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21 char formed in the catalyst during *ex-situ* CFP, because there is less reactant contacting the
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23 catalyst. Alternatively, heavy coke precursors may remain in the microreactor and
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25 contribute to char formation. When a catalyst is present at high temperature, these
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27 precursors may diffuse into the catalyst macropores and condense to form the higher
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29 temperature char.
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33 Interestingly, the dTG peak temperatures of the coke/char from both the *in-situ* and
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35 spouted-bed reactor are very similar. This may suggest that although the heating rate, C/B
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37 ratio, and residence time are all intrinsically different, the structure of coke and char are
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39 relatively unaffected.
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46 47 48 49 **4. Conclusions**

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51 The results of this study indicate that *in-situ* CFP in PyGC produced higher liquid yields
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53 and lower permanent gas yields compared to *ex-situ* CFP. Approximately the same amount
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55 of solid product was formed in each configuration. Reaction pathways for *in-situ* and *ex-*
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57 *situ* CFP are similar. However, the extent of these reactions was greater during *ex-situ* CFP.
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5 *Ex-situ* CFP in PyGC more accurately predicts the molecular composition of bio-oil
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8 produced by CFP in a bench-scale spouted-bed reactor. However, the char/coke formed by
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10 *in-situ* CFP had a nearly identical structure to that formed in the spouted-bed.
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17 **Acknowledgements**

18
19 This work was funded by NSF Award CBET-1236738. Funding for the research was also
20
21 provided by the NSF GK-12 Program (Award Number 0947869). The authors would also
22
23 like to acknowledge Dr. Anthony Provatas for his help with GC-MS, and W. R. Grace &
24
25 Co. for supplying the ZSM-5 catalyst used in this work.
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Configuration	<i>In-situ</i> CFP	<i>Ex-situ</i> CFP		Spouted-bed
		<i>Pyrolysis</i>	Upgrading	
Temperature [°C]	600	600	600	600
C/B ratio	1-10	-	1-10	1-5
WHSV [hr ⁻¹ *10 ⁵]	2	-	1-10	0.0006-0.00012
Flow rate [mL/min]	50	50	50	5000
Heating rate [°C/sec*10 ⁴]	2	2	10 [*]	10 [*]
Catalyst preheat	No	-	Yes	Yes
Catalyst bed length (height) [cm]	~0.5	-	0.026-0.26	2.5-5.3

Table 1. Operating conditions for *in-situ* CFP, *ex-situ* CFP and spouted-bed reactor

*Estimated based on reactor dimensions and operating condition. For example, in spouted-bed, the parameters for the calculation are the inlet diameter (0.635 cm), flow rate (5 L/min), temperature difference between inlet and catalyst particle (500 °C) and distance between inlet and catalyst particle (1 cm). This calculation does not consider the time for heat transfer between biomass particle and catalyst particle

Figure 1. PyGC results for *in-situ* CFP of miscanthus: A) Carbon yields to liquid products (red), permanent gas (blue), solid coke/char (green), and overall carbon balance (black, right axis); B) Permanent gas carbon yields for various C/B ratios; C) Carbon yields to liquid products.

Figure 2. PyGC results for *ex-situ* CFP of miscanthus: A) Carbon yields to liquid products (red), permanent gas (blue), solid coke/char (green), and overall carbon balance (black, right axis) for various C/B ratios; B) Permanent gas carbon yields for various C/B ratios; C) Carbon yields to liquid products.

Figure 3. A) Carbon yield of aromatic products including benzene, toluene, xylene, naphthalenes, indenes, and other PAHs for *in-situ* and *ex-situ* CFP; B) Carbon bio-oil selectivity of aromatic compounds for *in-situ* and *ex-situ* CFP.

Figure 4. Comparison of the overall product yields to bio-oil components, solids, and permanent gas for: A) *in-situ* CFP in PyGC; B) *ex-situ* CFP in PyGC; and C) CFP in spouted-bed reactor.

Figure 5. CO yield vs aromatic and oxygenate yield for pyrolysis of miscanthus using: (A,B) *in-situ* CFP in PyGC; (C,D) *ex-situ* CFP in PyGC; and (E,F) CFP in spouted-bed reactor.

Figure 6. A) Smoothed differential thermograms (dTG) of carbonaceous deposits collected from the *in-situ* and *ex-situ* CFP in PyGC and the spouted-bed reactor at 600°C; B) Smoothed dTG curves measured from solids deposited in the pyrolysis microreactor from *in-situ* CFP of miscanthus with unsupported ZSM-5 at C/B ratios of 2, 5 and 10.

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Experiment

Schematic

Liquid Analysis

1. Thermal
Pyrolysis

2. *In Situ* CFP
(1/1 C/B)

3. *In Situ* CFP
(10/1 C/B)

4. *Ex Situ* CFP
(1/1 C/B)

5. *Ex Situ* CFP
(10/1 C/B)

Biomass
Catalyst