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Pyrolysis and Catalytic Upgrading of Pinewood Sawdust Using an Induction Heating Reactor

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Supporting Information

ABSTRACT: The upgrading of pyrolysis bio-oil is an important process for obtaining stable, high-quality bio-oil. Rapid and uniform heating of both the biomass and the catalyst bed plays an important role in the product quality and in the overall process efficiency. Induction heating offers numerous advantages over conventional heating methods: rapid, efficient heating and precise temperature control. In this study, an advanced induction heating technology was tested for pyrolysis as well as catalyst bed heating. Three different catalyst-to-biomass ratios were studied (1:1, 1.5:1, and 2:1 weight basis), and the effect of catalyst bed temperature (290, 330, and 370 °C) was also investigated. The results were compared with conventionally heated catalyst bed reactor. Higher-quality bio-oil was obtained with induction heating reactor with increased yield of aromatic hydrocarbons and reduced oxygen content compared to conventional heating. Inductively heated catalyst was also observed to have lower carbon deposition after reaction, compared to conventionally heated catalyst. Higher Brunauer–Emmett–Teller (BET) surface area was available post-reaction for inductively heated catalysts. This observation could be attributed to higher thermal gradients in conventional reactors, which causes the condensation of molecules on the catalyst surface with cooler temperatures; these effects are less pronounced for the inductively heated catalyst.

1. INTRODUCTION

Research and development in the field of environmentally friendly biofuel production from renewable resources such as biomass has gained momentum in past few decades, because of the exhaustion of fossil energy sources and an ever-increasing population with its corresponding ever-increasing demand for energy. Among the technologies proposed, thermochemical treatment of biomass has gained considerable attention over the past few years, because of its ability to produce high-energy content fuel, with little or no overall environmental impact.[4,22,23] Thermochemical conversion involves breaking down biomass at elevated temperatures, followed eventually by catalytic treatment. Pyrolysis is a thermochemical process where dry, ground biomass is heated in the absence of oxygen at elevated temperatures (500–900 °C).[7] The gases thus formed are immediately quenched to obtain bio-oil. This pyrolytic bio-oil is a mixture of water, tar, and lighter organic liquid molecules.

Although the quality and quantity of bio-oil produced are dependent on biomass type, the pyrolysis method generally produces poor quality oil that is highly oxygenated.[6,32,33] Pyrolysis bio-oil has oxygen content of ~40%, which marks a major difference between pyrolysis fuel, and hydrocarbon (HC) fuel, which has an oxygen content of <1%.[10] High oxygen content leads to a decrease in energy density by 50%, compared to HC fuels; it also makes the bio-oil immiscible in HC fuel.[32] Other limitations associated with pyrolytic bio-oil include the unstable nature of the oil, high acidity, and high ash content, making the fuel undesirable. An efficient bio-oil upgrading technique is required to overcome these limitations.[32]

One of the most effective ways to reduce oxygen content of bio-oil is by thermocatalytic cracking.[25] In this process, pyrolysis vapors produced from thermochemical decomposition of biomass are passed over a hot catalyst bed that facilitates hydrodeoxygenation reaction (HDO). Oxygenated bio-oils are decomposed to lighter hydrocarbons over catalysts maintained at high temperatures, with the oxygen being removed in the form of water, CO_2, and CO.[18] It was reported that the use of catalysts such as Al-MCM-41, Cu/Al-MCM-41, and Al-MCM-41 with enlarged pores affect bio-oil composition.[1] Levoglucosan was eliminated, whereas the yield of furan, aromatics, and acetic acid increased. Adjaye and Bakshi studied the effect of five catalysts, namely, HZSM-5, H–Y, H-mordenite, silicate, and silica–alumina,[2] at four different temperatures: 290, 330, 370, and 410 °C. Highest yield of hydrocarbon was achieved with HZSM-5 catalyst. Overall, numerous studies have been performed over the years to study the effect of various catalysts on pyrolysis vapor upgrading, and zeolites such as HZSM-5 have proved to be one of the most effective catalyst for deoxygenation of bio-oil.[2]

Some of the major disadvantages of thermocatalytic upgrading of pyrolysis are coke deposition on catalyst that leads to catalyst deactivation, other problems associated with catalyst are poisoning by reactive species, and nonuniform heating of catalyst in the reactor.[10,32] Conventional heating have limitations due to slow heating rates, nonuniform heating, low energy efficiency, and safety concerns. Slow heating of the

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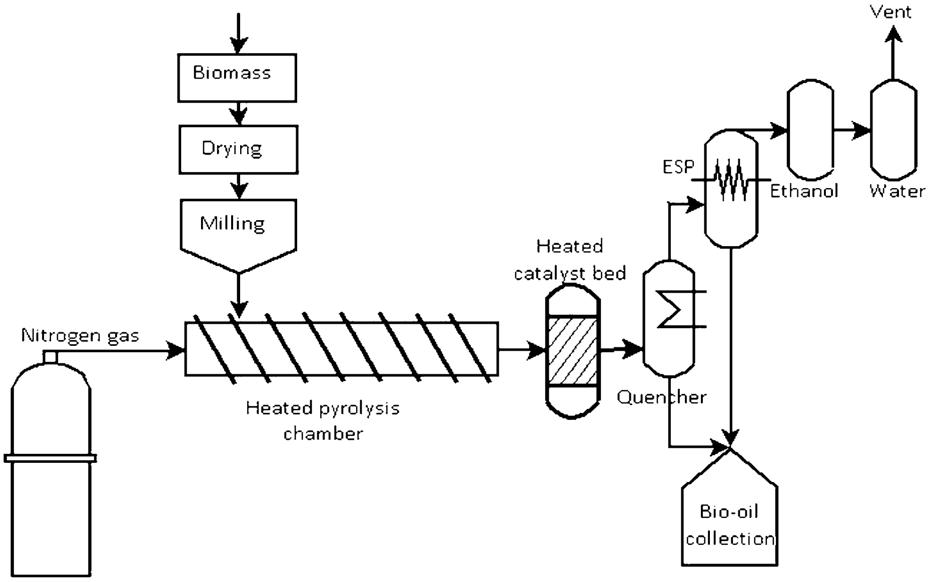

Figure 1. Flowchart for pyrolysis upgrading in an induction heater.

catalyst causes a temperature gradient, which may lead to catalyst fouling.

Induction heating or radio-frequency (RF) heating has the potential to overcome these issues, since it offers several key features, which make it promising as a pyrolysis and catalyst heating source: rapid heating rates, precise temperature control, and high energy efficiency.[16,29] Induction heating is a contactless heating method in which an AC power source is used to supply an alternating current to an induction heating coil. The coil generates an oscillating magnetic field at its core, which inductively heats a magnetic load (a material with a magnetic permeability of >0). Some studies have explored induction heating for the pyrolysis of biomass,[14,26−29] but these were mainly directed toward the production of char and bio-oil without upgrading. However, there generally has been very little work published on this method; therefore, this technique needs further study to establish its use and practicality. This study was conducted to fill these knowledge gaps and to test an induction heating pyrolysis reactor's ability to produce bio-oil both with and without a catalytic bed from pine sawdust.

To our knowledge, this is the first reported study in which an induction-heating reactor was used for biomass pyrolysis, as well as for heating the catalyst bed for catalytic upgrading of pyrolysis vapors. The induction-heated catalyst results were compared to conventional heating of the catalyst using a heating tape to study the quality of oil and the catalyst performance. By comparison, the above-mentioned studies[14,26−29] did not use induction heating as a method to further refine the pyrolysis bio-oil into a deoxygenated product. Thus, our study provides valuable insights into the behavior of deoxygentation catalysts when heated with electromagnetic fields (more specifically, induction-based RF heating), insights hitherto unavailable in the research literature.

2. MATERIALS AND METHODS

2.1. Materials. Pine sawdust from scrap wood out of the wood shop at Louisiana State University was used as a model biomass for preliminary pyrolysis experiments. Pinewood sawdust is the most commonly used biomass for pyrolysis, and abundant data are available in the literature for comparison; hence, this biomass was chosen for the present study. The sawdust was grinded and its moisture content was measured. The H-ZSM5 (Si/Al ratio 38) catalyst was obtained from ACS Materials (Medford, MA). Pyrolysis and upgrading experiments were conducted in two separate induction-heating machines. The biomass was pyrolyzed in a low-frequency RDO induction heater (RDO Induction LLC, Washington, NJ) that operated in the frequency range of 35−100 kHz and used a power supply of 5 kW. The reaction tube was a 310 stainless steel triclamp tube that had a length of 419 mm and an inner diameter of 34.4 mm. The system was purged of oxygen using nitrogen gas at the flow rate of 1 L/min for 20 min. Nitrogen was supplied by Air Liquide (Houston, TX). The induction coil used was a ten-loop rubber coated copper coil with an overall length of 285 mm and an inner diameter of 59 mm. The reaction tube temperature was controlled using a calibrated Omega IR2C series infrared feedback controller (Omega, Stamford, CT). For the upgrading reaction, the catalyst was heated in a 5.0 kW RDO induction heater operating at higher frequencies (in the range of 135−400 kHz) (RDO Induction LLC, Washington, NJ). The reaction tube was a 310 stainless steel triclamp tube that had a length of 270 mm and an inner diameter of 25.4 mm. The reaction tube temperature was controlled using a calibrated Raytek M13 series infrared remote temperature sensor (Raytek Corporation, Santa Cruz, CA) coupled with a proportional−integral−derivative (PID) controller (Red Lion Controls, Inc., York, PA). The bio-oil collection system consisted of an electrostatic precipitator (ESP) that was built in-house and a 500 mL flask suspended in an ice bath. The flowchart of the pyrolysis system is shown in Figure 1 with the catalyst bed being removable for the noncatalyzed experiments. The heating tape for conventional heating experiment was a 13 mm × 1220 mm high-temperature heavy insulated heating tape with 313 W output operating at 120 V (Briskheat Corporation, Columbus, OH). The temperature of the heating tape was controlled using a SDC benchtop temperature controller with a Type K thermocouple (Briskheat Corporation, Columbus, OH).

2.2. Procedure. Two sets of experiments were designed and performed. Preliminary experiments were conducted for testing various parameters for pyrolysis in induction heater and setting the basis for secondary upgrading experiments. The results from secondary upgrading experiments using induction heaters were compared with catalysts that were heated conventionally.

2.2.1. Preliminary Experiments. Since a metallic Type K thermocouple cannot be used to measure the temperature inside the catalyst bed, an infrared thermocouple was used to measure the temperature of the pipe surface. Preliminary experiments were conducted in order to determine the true biomass and catalyst temperature inside the pipe. The pipe was loaded with char from previous runs, and a temperature of 500 °C was set on the controller. Char was used, to avoid the formation of pyrolytic gases at the exit. As soon as the set temperature was achieved, the induction heater was switched off and a regular Type K thermocouple was inserted inside the pipe.

The temperature recorded by this Type K thermocouple was recorded using a PicoLog temperature data logger (Model TC-08 data logger, Pico Technology, Tyler, TX) and compared to the data from the infrared remote sensor to identify any discrepancies. The difference in the two readings was <5 °C (≤1%); thus, for all subsequent experiments, the biomass temperature was assumed to be the same as that of the outside pipe temperature recorded by the infrared remote sensor for the given setup.

Total reaction time at the respective temperatures was determined for the sawdust by performing pyrolysis experiments for different time intervals spanned at 10 min intervals, and weighing the char residue. A 25 g biomass sample was heated in the induction heater at a particular temperature. The temperature was maintained for 10 min and then the system was allowed to cool. The weight of the biomass char residue was recorded. This was repeated until the change in weight of the char residue was negligible. The time at which the char weight remained unchanged from the previous experimental run was considered to be the optimal time required for complete reaction.[12]

2.2.2. Pyrolysis of Pine Sawdust without Upgrading. A 30 g sample of finely grinded sawdust was placed in the induction pyrolysis reactor. The system was purged for 20 min with nitrogen gas before heating. Pyrolysis was carried out at five different temperatures from 500 °C to 700 °C, in 50 °C increments. The vapors thus produced flowed out of the reaction chamber and into the collection system, which was equipped with an ice bath (for condensation) and an electrostatic precipitator.[12]

2.2.3. Secondary Upgrading Experiment. All upgrading experiments were carried out at three different temperatures (290, 330, and 370 °C) using HZSM-5 catalyst with pyrolysis itself at 600 °C. The vapors obtained from reactor-1 (biomass induction pyrolyzer) were passed over an HZSM-5 catalyst inside a 25.4 cm ID stainless tube. The catalyst pellets (ϕ2 mm × 2−10 mm) had a pore volume of ≥0.25 mL/g, a bulk density of ~720 kg/m^3, a specific surface area of ~250 m^2/g, and a pore size of ~5 Å. The tube was heated using the second induction heater. Three catalyst-to-biomass ratios (C/B) were studied: 1:1, 1.5:1, and 2:1. The same catalyst was used twice (run 1 and run 2) for each ratio and temperature combination as two separate experiments, to study the extent of deactivation and coke deposition of catalyst. Reproducibility was tested by duplicating each of run 1 and run 2 under all conditions. A heating tape was used to maintain the temperature between two induction reactors at 200 °C, to avoid inline condensation. The resulting upgraded vapors were condensed in a round-bottom flask that had been placed in an ice bath, followed by the electrostatic precipitator to collect the remaining condensable gases. The system was allowed to cool for 40−50 min. Liquid was drained in a glass vial, weighed, and stored at −20 °C to avoid further polymerization reactions during storage. The incondensable gases were passed through an ethanol and water trap before being vented (Figure 1) with samples being collected in gas sample bags. The char and catalyst were also collected, weighed, and stored.

The results were compared with conventional catalyst bed heating method using the heating tape wrapped around the tube. A benchtop temperature controller was used to maintain the catalyst bed temperature measured using a Type K thermocouple. Control experiments were carried out for a C/B ratio of 2:1 at three different temperatures (290, 330, and 370 °C). Based on the results obtained from the induction heating reactor, this C/B ratio was the most effective; hence, only this ratio was chosen for the conventional heating experiments. The catalyst was rerun in the reactor to study the extent of deactivation. The bio-oil and catalyst quality was compared with the induction heating experiments.

2.2.4. Product Characterization. Liquid, gas, and char yields were quantified for both primary and secondary experiments. Coke yield was quantified for secondary upgrading experiments based on the initial and final weight of the catalyst. Yields were calculated based on initial biomass weight, and the gas weight was calculated from the percentage difference of liquid, char, and coke yield. Oil and char samples were analyzed for carbon, hydrogen, nitrogen, and oxygen (CHNO) content, using a Perkin−Elmer Model 2400 elemental analyzer, as previously described.[19] Liquid samples were also studied for water content using Karl Fischer titration, the product composition of the aqueous and organic phases were studied via gas chromatography−mass spectroscopy (GCMS) using a Varian 1200 series system with a DB5 capillary column and a Wiley 6N library for product identification, and the area under the peak was integrated for product composition. The surface of the catalyst was characterized using different techniques to investigate the extent of coking and deactivation. X-ray diffraction (XRD) was used to determine the presence of internal coke in the catalyst, using an Empyrean X-ray Diffractometer (PANalytical, Westborough, MA).[15] X-ray photoelectron spectroscopy (XPS) was used to identify and quantify the different elements present in the catalyst, using a Kratos Axis 165 X-ray photon spectroscopy/auger electron spectroscopy (XPS/AES) system that was operated with a monochromatic Al Kα X-ray source with a beam current of 10 mA and HT at 12 kV. Catalyst surface area and pore volumes were measured with a BET surface analyzer (NOVA, 2200e Series) and a surface area and pore size analyzer using nitrogen adsorption (Quantachrome Instruments, Inc., Boynton Beach, FL). Temperature-programmed desorption of ammonia (NH_3-TPD) analysis was carried out using a chemisorption apparatus (Micromeretics, Model 2700), according to the procedure described by Lee et al.[13] Briefly, 0.05 g of a prepared sample was loaded in the U-tube and degasses with helium gas at 500 °C for 30 min. The sample was then cooled to 100 °C and saturated with ammonia. NH_3-TPD measurements were recorded from 100 °C to 500 °C. The coke deposition on the catalyst was determined using CHN elemental analysis of the spent catalyst (Perkin−Elmer, Series 2400, Waltham, MA).[3] Fourier transform infrared (FTIR) spectroscopy of the catalyst was performed to determine the chemical composition of coke that had been deposited on the catalyst surface.[15]

3. RESULTS

3.1. Biomass Properties. The physical and chemical properties of biomass used in the pyrolysis have a significant impact on the quality of the bio-oil produced.[17] Pinewood sawdust used in our experiments was tested for moisture content determination, elemental analysis to determine CHN content, and thermogravimetric analysis (TGA) (Figure 2a). The moisture content was performed using a Mettler Toledo LD 16 system, and it was determined to be 5.37% ± 0.12%. Knowledge of biomass moisture content is important, because it shows partially where water in the liquid product comes from, and it may also act as a stabilizing agent during the pyrolysis reaction.[11] The elemental analysis (Table 1) shows the presence of carbon, hydrogen, and nitrogen in the biomass feedstock. The biomass density obtained from literature was 0.168 g/cm^3.[8] The TGA of the biomass (Figure 2a) shows the percentage of pine sawdust remaining, with respect to the change in temperature. This gives a practical idea of which temperature would maximize the biomass decomposition. The majority of the loss of mass occurs at 380 °C and then follows a slight decline until the reaction temperature reaches 800 °C. At that temperature, the biomass is reduced to its nonreactive ash content. This shows us that a temperature range of 380−800 °C allows for the maximum conversion of biomass, and the range used for the pyrolysis (500−700 °C) fits into this range of optimum biomass conversion.[23]

3.2. Pyrolysis Yield. Figure 2 shows a comparison of liquid, char, gas and coke yield between the nonupgraded and upgraded experiments. Since no catalyst was involved in nonupgraded process, the coke content for the non-upgraded

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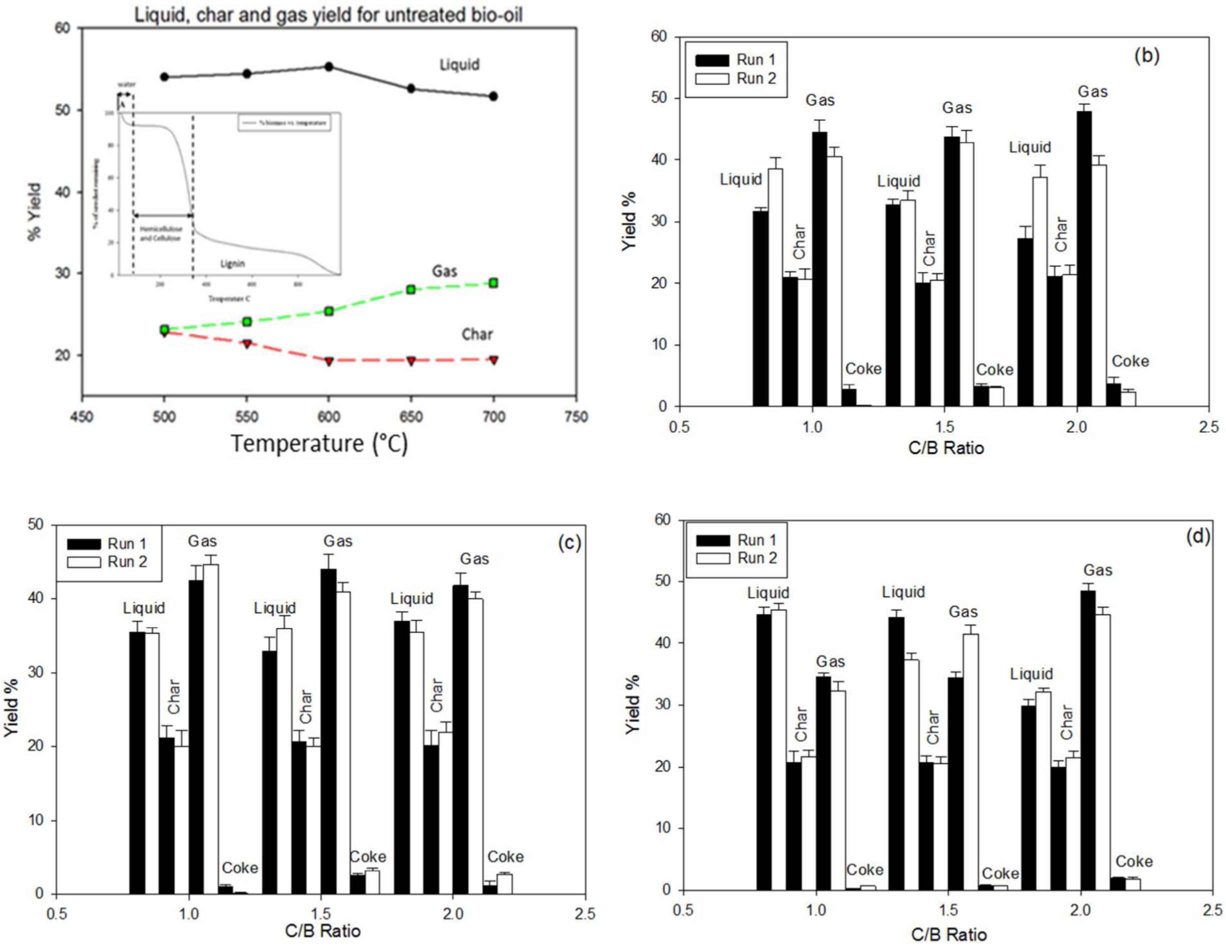

Figure 2. Pyrolysis liquid, char gas, and coke yield data for (a) pyrolysis without catalyst along with TGA analysis, (b) yields at 290 °C for different C/B ratios, (c) yields at 330 °C for different C/B ratios and, (d) yields at 370 °C for different C/B ratios.

experiment was not determined. All product yields were calculated on the basis of mass.

3.2.1. Non-upgraded Bio-oil. The composition of the pyrolysis yields (non-upgraded) followed expected trends shown in numerous works described in the literature.[4,7,24] Char yields decreased as the temperatures increased, because of the more complete decomposition of the biomass achieved at higher temperatures. The maximum char yield was 22.86%, and it was obtained at the lowest reaction temperature (500 °C). The gas yields increased at higher temperatures as a more thorough breakdown of the biomass occurred, yielding lower molecular mass products. The highest gas yield was achieved at 700 °C with 28.81% of the biomass converted to non-condensable gases. The liquid yields increased to a maximum and then decreased as the temperature increased, with the maximum yield of 55.28% being achieved at 600 °C (Figure 2a).[12] For the upgrading experiments, pyrolysis was conducted at this temperature.

3.2.2. Upgraded Bio-oil. Figures 2b, 2c, and 2d show the liquid, char, gas, and coke yield for three different C/B ratios (namely, 1:1, 1.5:1, and 2:1) for three different catalyst bed temperatures (290, 330, and 370 °C, respectively). Run 2 represent the experiments with the same catalyst as used in Run 1, without any regeneration. The general observation is that liquid yield decreases when biomass vapors are catalytically upgraded, compared to non-upgraded process. The overall decrease in liquid yield was ~10% when pyrolysis vapors were upgraded over a heated catalyst. Liquid yield reduced from 50%−55% for no upgrading to 35−45% after catalytic upgrading. It is observed that highest liquid yield was achieved at highest catalyst bed temperature, with a maximum yield of 45.43% at 370 °C and C/B ratio of 1:1 in Run 1. The lowest liquid yield was 27% at 290 °C and C/B ratio of 2:1 in run 1. These results were consistent with those reported in the literature.[2] The liquid yield mostly increased when the catalyst was reused for Run 2, with the exception of 330 °C, with a C/B ratio of 2, and 370 °C, with a C/B ratio of 1.5. The increase in yield for Run 2 could be due to coke deposition on the catalyst surface partially deactivating the catalyst. This deactivated catalyst does not support the cracking reaction, and the liquid

Table 1. CHN Composition of the Char Product of the Noncatalyzed Pyrolysis Reactitalyzed Pyrolysis Reaction and the Unburned Biomass

reaction temperature (°C)	Composition (%)		
	carbon	hydrogen	nitrogen
unpyrolyzed sawdust	46.63 ± 0.03	6.43 ± 0.00	0.20 ± 0.00
500	81.19 ± 0.01	3.50 ± 0.00	0.34 ± 0.00
550	86.00 ± 0.005	3.09 ± 0.00	0.37 ± 0.001
600	88.50 ± 0.01	2.44 ± 0.00	0.53 ± 0.00
650	89.70 ± 0.012	2.01 ± 0.00	0.75 ± 0.00
700	88.52 ± 0.014	1.89 ± 0.00	1.46 ± 0.001

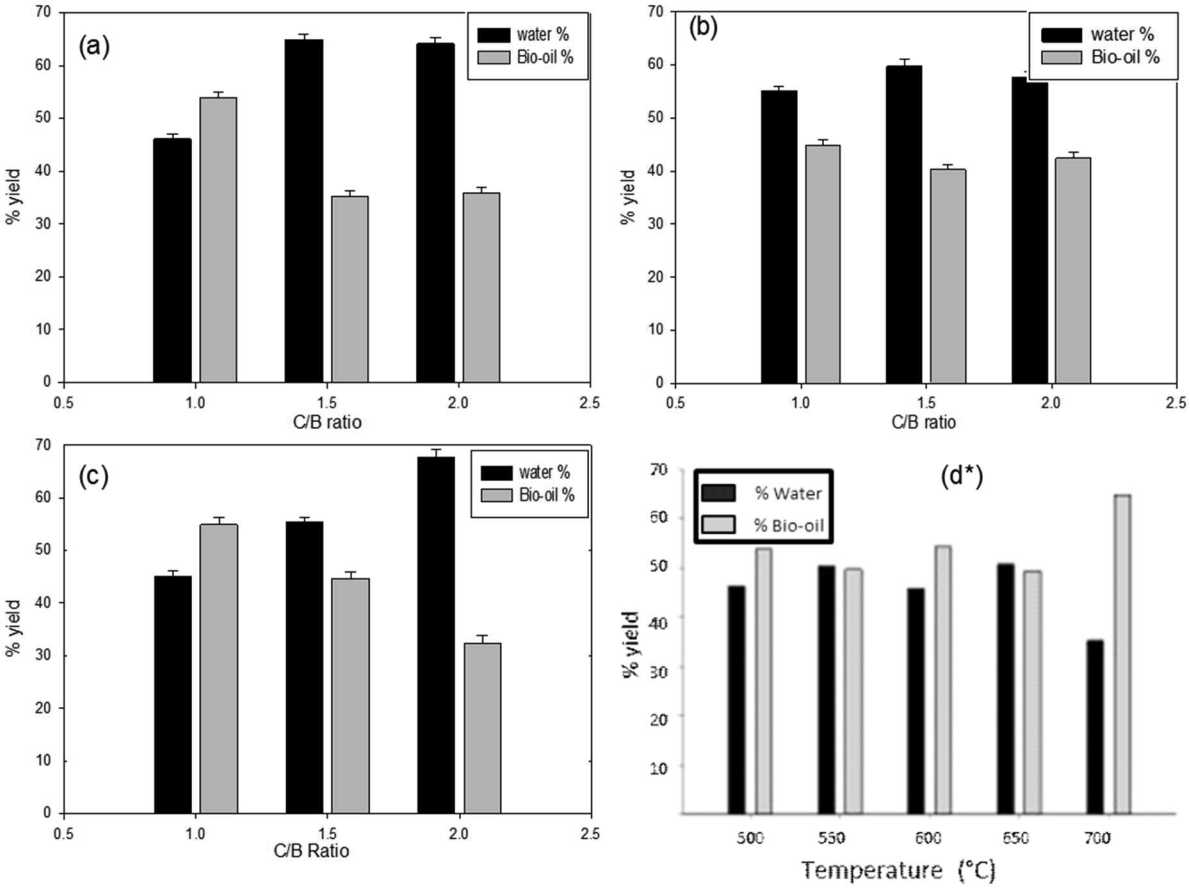

Figure 3. Water content and bio-oil yield of pyrolysis bio-oil from pinewood sawdust at a) 290 °C at different C/B ratio, b) 330 °C at different C/B ratio, c) 370 °C at different C/B ratio and, (d) non-upgraded bio-oil at different temperatures.

yield increases, which is an observed trend for reactions without catalytic upgrading. The exception at 370 °C with a C/B ratio of 1.5 is rather significant; however, the reason is unknown. The liquid yield also decreases as the C/B ratio increases at all temperatures. For higher C/B ratios, high-molecular-weight compounds are broken down to lower fractions and gases more often as more catalyst surface is available for reaction. This also explains the increase in gas yield with increasing C/B ratio. The coke yield was measured from the difference in the initial and final weight of catalyst after each run and was consistent with the elemental analysis of catalyst, which is discussed elsewhere in this paper (see section 2.2.4, "Product Characterization"). The highest coke deposition was observed at the highest C/B ratio and the lowest temperature. No significant change in bio-oil yield was observed when the catalyst bed was heated using conventional heating and an induction heater (see Table S1 in the Supporting Information).

3.3. Water Content of Bio-oil.

3.3.1. Non-upgraded Bio-oil. Figure 3 compares the organic fraction and the water fraction found in the liquid product. The amount of water found in the liquid bio-oil product is consistently between 40% and 55% for all samples, the lowest water percentage of 32.23% occurring at 700 °C (Figure 3d); this indicates that, while the overall liquid yield may be lower at the higher pyrolysis temperatures, the quality of the oil may be slightly improved.[12]

3.3.2. Upgraded Bio-oil. Catalytic upgrading removes oxygen in the form of water, carbon dioxide, and carbon monoxide, which is the reason why the water content of upgraded bio-oil is higher than that of non-upgraded bio-oil.[2] The amount of water increased as the amount of catalyst increased for all temperatures as expected, as more oxygen was removed in the form of water. No specific trend was observed between different temperature ranges. The increase in water content for upgraded bio-oil was ~15%–20%, compared to non-upgraded bio-oil, depending on the amount of catalyst. The difference in water content of liquid fraction for the two type of catalyst heating methods, namely, conventional heating and induction heating, was <5%, concluding that neither liquid yield nor water content was significantly affected when the method of heating the catalyst was changed (see Table S1).

3.4. Elemental Analysis.

3.4.1. Sawdust and Char. An elemental analysis was performed on the sawdust and char samples of the pyrolysis reactions. The percentage of carbon, hydrogen, and nitrogen were studied (Table 1). Nitrogen values were negligible for all samples. The carbon content increased from 46.63% for pure sawdust to 81%–86% for char, depending on the reaction temperature, while the hydrogen content decreased from 6.43% for unpyrolyzed sawdust to 1.89% for char at a pyrolysis temperature of 700 °C. Hydrogen values for char decreased as the pyrolysis temperature increased. The carbon content for char increased as the temperature increased. This is an indication that the biomass was more thoroughly reduced at the higher temperatures;[22] this is also supported by the char yield data. The pyrolysis reaction itself can be understood as a series of reactions that leave behind an increasingly condensed carbon matrix.[22] The removal of the more reactive hydrogen was increased at the

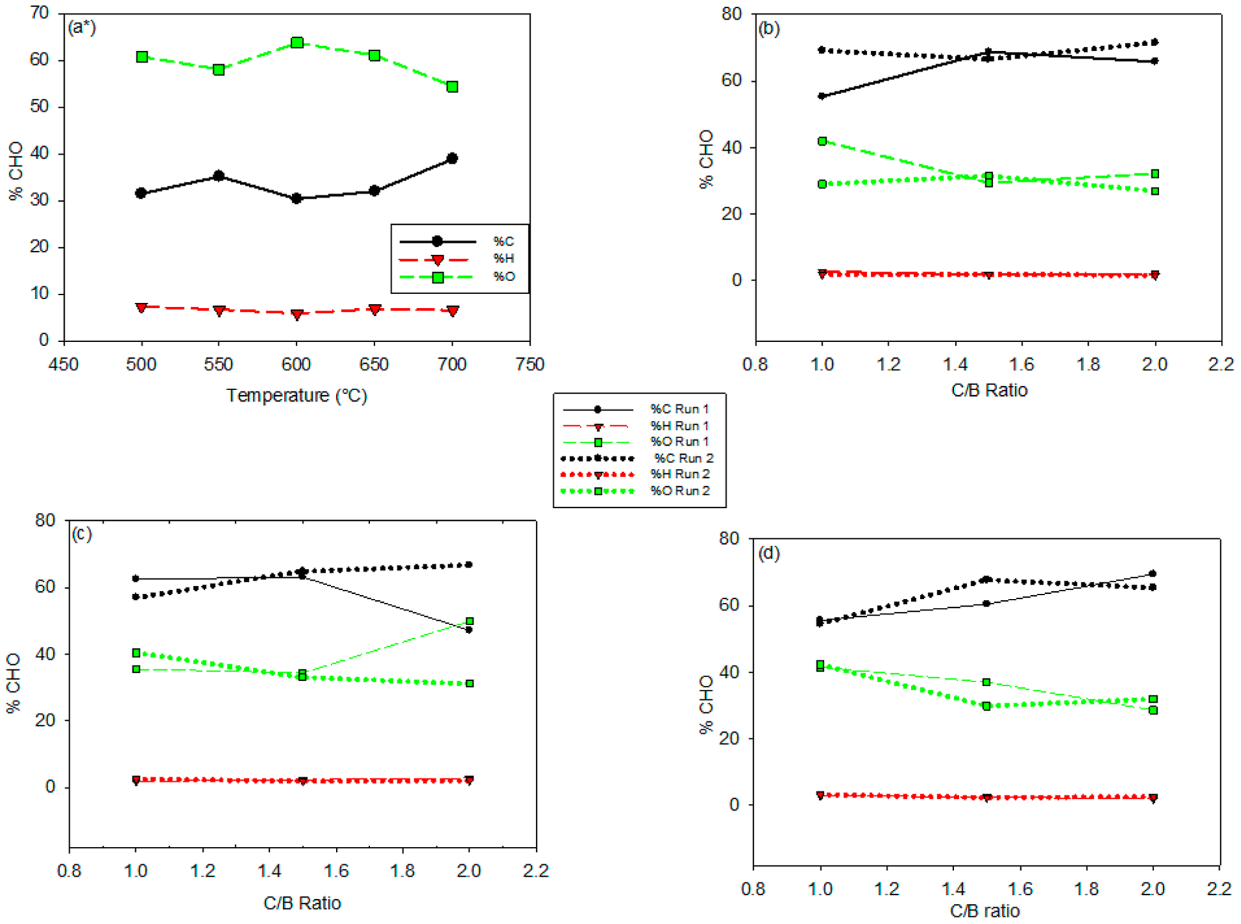

Figure 4. Change in the amount of carbon, hydrogen, and oxygen (as a percentage) for (a) untreated bio-oil and catalyst temperatures of (b) 290 °C, (c) 330 °C, and (d) 370 °C.

higher temperatures, while the more stable carbon was left unvolatized in the absence of oxygen.[12]

3.4.2. Non-upgraded Bio-oil. Figure 4a shows the carbon, hydrogen, and oxygen (CHO) content for bio-oil without catalyst treatment. The carbon content of the bio-oil yield shows little relation to temperature, which could be attributed to the variation in the water content and volatility of bio-oil samples.[12]

3.4.3. Upgraded Bio-oil. Figures 4b–d also show CHO analysis of the upgraded bio-oil samples. The oxygen content of the bio-oil was reduced from 45%–60% to 25%–30% for almost all temperature and C/B ratio combinations. Some discrepancies could be due to machine error, or error due to mass changes. Many compounds in the bio-oil have a tendency to volatize at room temperature; this fact made it rather difficult to maintain a constant weight for elemental analysis. A general trend was observed whereby the oxygen content decreased as the C/B ratio increased. No specific relation was observed, with respect to temperature or heating method (see Table S1).

3.5. Product Composition. Gas chromatography was used for identifying the product composition of the bio-oil using integration of area under corresponding peaks (Table 2). Non-upgraded bio-oil was mostly composed of phenols and aldehydes with some concentration of ketones, alcohols, and acids with aromatic compounds detected in insignificant amounts.[12] This is a typical observation for bio-oil obtained from the pyrolysis of biomass. This bio-oil is generally rich in oxygenated hydrocarbons, such as phenols.[2,18]

Table 2. Product Composition and Yield for Pyrolysis Bio-oil with and without Upgrading

		with catalyst (%)	
compound	no catalyst (%)	inductive heating	conventional heating
ketones	9.78	2.79	0.928
aldehydes	13.60	5.56	1.55
alcohols	3.03	5.76	0.56
acids	1.38	1.08	4.35
phenols	53.41	30.45	33.1
furfural	8.34	7.54	12.5
aromatics		32.02	25.01
benzene		11.03	
methylbenzene		0.36	4.05
ethylbenzene		0.32	0.684
xylenes		4.49	7.92
C_9–C_{10}		14.54	12.356
naphthalenes		12.06	10.4
olefins		0.25	
unidentified	10.46	3.77	11.602

The use of a catalyst produces a higher yield of non-oxygenated hydrocarbons, such as aromatic hydrocarbons (C_5–C_{10}). These hydrocarbons have a higher octane number (comparative to those of petroleum fuel) and are of interest for fuel replacement and additives. Moreover, an aromatic yield of ~32.02% is obtained for an inductively heated catalyst, whereas for a conventionally heated catalyst, the aromatic yield

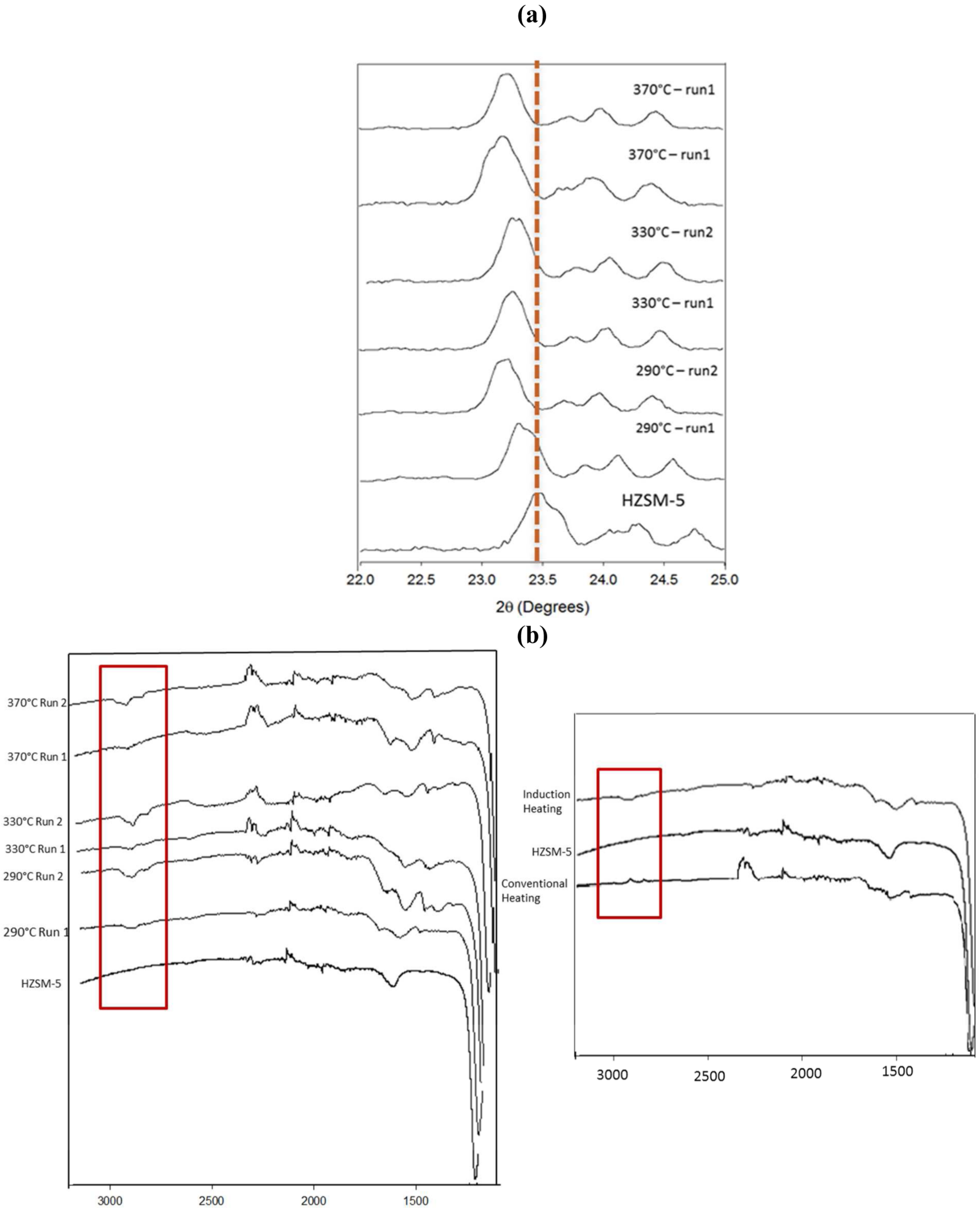

Figure 5. XRD pattern for C/B ratio of 2:1 for (a) fresh and coked catalyst after induction heating reaction. (b) FTIR analysis of fresh and used catalysts.

was 25%, indicating superior upgrading performance of the inductively heated catalyst (Table 2).

3.6. Catalyst Analysis. Since a C/B ratio of 2:1 gave the highest yield for aromatic compounds, this set was chosen for analysis. A total of 12 catalyst samples from pinewood sawdust pyrolysis upgrading with a C/B ratio of 2:1 were analyzed. The catalysts in the reactor were heated at three different temperatures; 290, 330, and 370 °C. The catalyst samples for run were fresh catalysts, which were reused for the subsequent rerun in Run 2. Pure HZSM-5 was also analyzed for comparison. Catalyst heated via the conventional heating method was also analyzed for comparison for the same reaction setup.

3.6.1. X-ray diffraction (XRD) Analysis. XRD analysis was performed on the catalyst samples to determine if the coke deposition was present inside the catalyst. XRD patterns of

Table 3. Elemental Analysis (CHNS) for Fresh and Coked Catalyst for a C/B Ratio of 2:1

upgrading temperature (°C)	sample	carbon (%)	hydrogen (%)	nitrogen (%)	sulfur (%)
HZSM-5		0.2 ± 0.02	0.38 ± 0.09	0.18 ± 0.04	0.00 ± 0.00
Induction Heating					
290	Run 1	12.67 ± 0.19	1.09 ± 0.06	0.03 ± 0.00	0.01 ± 0.00
290	Run 2	7.89 ± 0.00	0.67 ± 0.11	0.00 ± 0.00	0.00 ± 0.00
330	Run 1	5.90 ± 0.08	0.12 ± 0.01	0.1 ± 0.01	0.00 ± 0.00
330	Run 2	7.89 ± 0.08	0.30 ± 0.02	0.06 ± 0.00	0.00 ± 0.00
370	Run 1	6.12 ± 0.03	0.61 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
370	Run 2	6.68 ± 0.02	0.29 ± 0.11	0.13 ± 0.05	0.00 ± 0.00
Conventional Heating					
290	Run 1	13.63 ± 0.01	1.98 ± 0.09	0.07 ± 0.00	0.00 ± 0.00
290	Run 2	20.25 ± 0.04	1.7 ± 0.10	0.07 ± 0.00	0.00 ± 0.00
330	Run 1	13.77 ± 0.38	1.19 ± 0.05	0.06 ± 0.00	0.00 ± 0.00
330	Run 2	11.63 ± 0.13	0.7 ± 0.18	0.04 ± 0.01	0.00 ± 0.00
370	Run 1	12.83 ± 0.04	0.85 ± 0.09	0.05 ± 0.02	0.00 ± 0.00
370	Run 2	8.58 ± 0.05	0.36 ± 0.005	0.03 ± 0.02	0.00 ± 0.00

coked catalyst were compared to the fresh catalyst. Figure 5a shows XRD pattern for fresh and coked catalyst in the 2θ range of 22°−25°. The peak for the used samples shifted slightly to the left, with the difference in angle being ~0.2°. Two adjoining peaks were observed for fresh HZSM-5 at $2\theta = 23.5°$ and 23.7°, respectively. These peaks were observed with lower intensity for catalyst samples heated at 290 °C but were not observed for 330 and 370 °C samples. An increase in intensity was also observed for all coked catalysts compared to fresh HZSM-5 especially for 330 °C (Run 2) and 370 °C (Run 2). A change in peak position was also observed for the coked catalyst with peaks at $2\theta = 24.3°$ and 24.7° for fresh catalyst. This change in intensity and position of subsequent peaks is a result of carbon deposition into the catalyst pores, which causes distortion of the zeolite lattice structure.[15]

3.6.2. FTIR Analysis. In order to study the chemical nature of coke, FTIR analysis of both fresh HZSM-5 and used catalyst was undertaken. FTIR analysis is used to study the surface chemistry and reactivity of a catalyst. With coke deposited on the surface, FTIR spectra help to determine the type of carbon bonds within a certain wavenumber range. Although the wavenumber range studied was 0−3500 cm^{-1}, the range of only 1200−3200 cm^{-1} is shown in Figure 5b, because it is the most relevant. Three important bands between 2800 and 3000 cm^{-1}, corresponding to aliphatic compounds $\equiv CH$, $=CH_2$, and $-CH_3$, were observed for all catalyst samples, except for the fresh catalyst. The dip is especially sharp for reused catalyst samples at all temperatures. The decrease in intensities for each reused sample could be because the coke turns polyaromatic in nature.[21] With time, the coke becomes more hydrogen deficient, which changes its nature from aliphatic to aromatic or polyaromatic. Another sharper dip (at ~1600 and 1700 cm^{-1}) is observed for catalyst samples at 290 °C (Run 1) for both inductively heated and conventionally heated catalyst but is missing from HZSM-5. This is another characteristic coke band, which indicates the presence of polyalkalene or polyaromatic compounds.[15]

3.6.3. Elemental Analysis. Elemental analysis was also performed on the catalyst to quantify the carbon, hydrogen, nitrogen, and sulfur content of the samples. All samples were corrected based on elemental analysis reading from pure HZSM-5 (Table 3). The results were consistent with those obtained from XPS. Carbon deposition decreased as the upgrading process temperature increased. A higher carbon percentage was observed for the conventionally heated catalyst (13%−20% at 290 °C), compared to the inductively heated catalyst (7%−12% at 330 °C). Hydrogen, nitrogen, and sulfur values were negligible.

These results highlight the improved performance of the inductively heated catalyst over conventional methods.

3.6.4. Surface Area and Pore Volume. Table 4 shows the surface area and volume for micropores. The BET surface area and pore volume of the catalyst showed significant decreases in surface area for the used catalyst, compared to pure HZSM-5 catalyst. The micropore volume also decreased. No specific trend was observed, with respect to temperature. The decrease in surface area is consistent with the increase in coke content of the catalyst. Less surface area is available for Run 2 (reused catalyst) at each temperature.

Table 4. BET Surface Area and Volume of Fresh and Coked Catalyst for a C/B Ratio of 2:1

sample		BET surface area (m^2/g)	micropore area (m^2/g)	micropore volume (cm^3/g)
HZSM-5		247.7	196.4	0.0950
Induction Heating				
290 °C	Run 1	197.0	0.0	0.0000
290 °C	Run 2	152.5	99.0	0.0490
330 °C	Run 1	179.8	120.7	0.0590
330 °C	Run 2	25.1	60.0	0.0280
370 °C	Run 1	210.7	143.4	0.0700
370 °C	Run 2	85.5	156.3	0.0690
Conventional Heating				
370 °C	Run 1	177.624	105.203	0.047
370 °C	Run 2	91.186	50.00	0.022

For the temperature of 370 °C, more surface area is available when the catalyst is heated using induction heating, compared to the conventionally heated catalyst.

3.6.5. NH_3-TPD Analysis. NH_3-TPD analysis helps to determine the extent to which deactivation of the catalyst has occurred and helps draw the mechanism of hydrocarbon conversion as the deactivation proceeds. Coking can affect the catalyst activity in two major ways. Depending on the nature of the coke deposited on the catalyst, the coke may poison the catalyst, or coke deposition may simply block the active sites and block the catalyst pores. Ammonia is a smaller-sized molecule and can diffuse through smaller pores or partially blocked pores. This NH_3-TPD technique can be useful in determining the effect of coking on the strength of acid sites. Two distinct peaks for fresh HZSM-5 are observed in Figure 6. The one that is observed at lower temperature represents weak acid sites and the one that is observed at higher temperature represents strong acid sites.

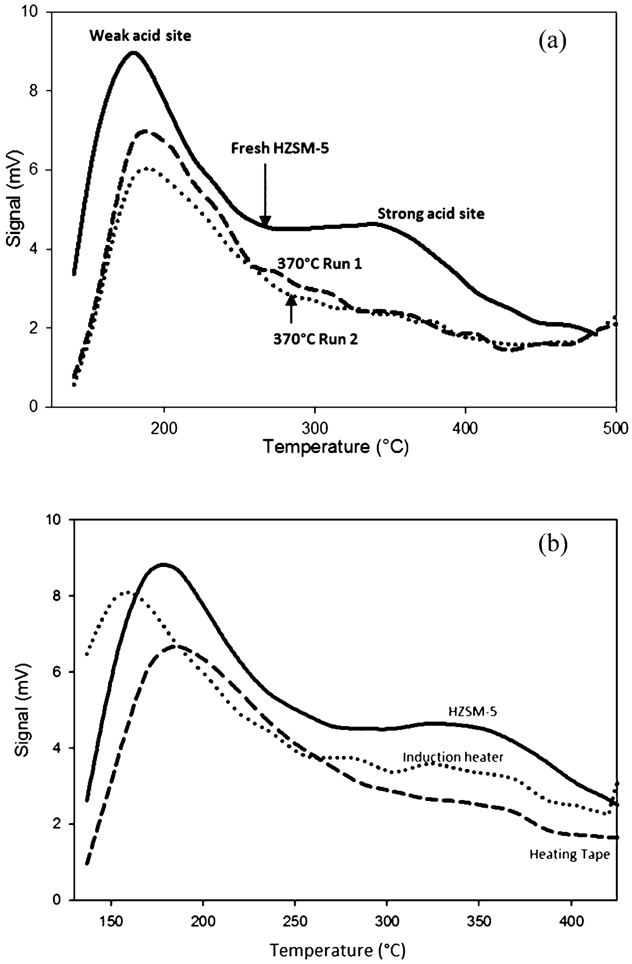

Figure 6. NH_3-TPD profile for a C/B ratio of 2:1 for (a) a fresh and inductively heated catalyst and (b) a fresh, inductively and conventionally heated catalyst.

The peak at higher temperature seems to slowly disappear for both samples at 290 °C, which means that coke deposition occurs mainly on strong acid sites. Weak acid sites are also consumed, but the rate of consumption is lower, compared to that of strong acid sites. The slight shift of the peak toward the left also indicates a decrease in the strength of acid sites, because of coke deposition. The peaks are smaller for reused samples, compared to samples from Run 1. Overall, the greater the coke deposition, the lower the peak area. These results are consistent with other studies reported in the literature for HZSM-5 catalyst behavior over time.[15] Figure 6b shows a comparison of the peak for the fresh catalyst to that with a conventionally heated catalyst and an inductively heated catalyst. The strong acid sites are observed to completely disappear for the conventionally heated catalyst, compared to the inductively heated catalyst. The weak acid site peak is also comparatively lower. These results are consistent with the catalyst's aromatization activity. The stronger the acid site, the greater the aromatization, and ZSM-5 has a greater concentration of strong acid sites.[31]

3.6.6. X-ray Photoelectron Spectroscopy (XPS) Analysis. X-ray photoelectron spectroscopy (XPS) is a quantitative surface chemical analysis technique that measures the elemental composition of the material.[9] All catalyst samples were ground and dried to remove any moisture absorbed. The XPS analysis was represented in the carbon-to-silicate (C/Si) ratio (mass basis). Since the zeolite has a constant silicate-to-aluminum ratio (Si/Al), the amount of silicate does not change. The change in C/Si ratio is only attributable to the occurrence of carbon due to coke deposition on catalyst. The occurrence of a carbon peak in XPS measurement is due to coke deposition on the catalyst surface. However, some carbon traces are also observed on pure HZSM-5, which could be due to some cross contamination from other samples. Figure 7 shows the C/Si ratio for fresh and used catalysts. The C/Si ratio was higher for a catalyst heated in a conventional heater; also, a higher C/Si ratio was observed at lower temperatures. For the inductively heated catalyst, the ratio did not vary significantly (correlation coefficient of $R^2 = 0.9$). Coke formation on acid catalysts such as that of HZSM-5 is strongly governed by dehydrogenation and cracking reactions. These reactions break the long-chain polymers to form aromatic compounds.[5] However, at lower temperatures, some organic molecules may condense on the cooler catalyst surface; this phenomenon is more prominent for nonuniformly heated catalyst surfaces, where the molecules may condense on cooler zones.

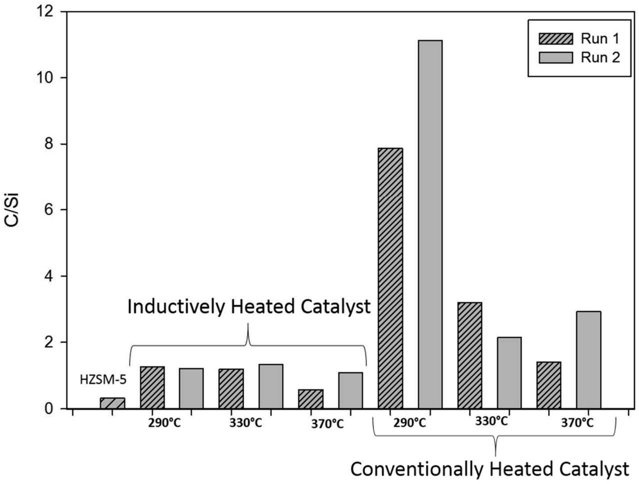

Figure 7. C/Si ratio for catalyst samples, as determined via XPS analysis.

One of the reasons for high amount of carbon obtained on conventionally heated catalyst could be a result of the condensation of molecules on the cooler sections of the catalyst surface, which is due to nonuniform heating.

3.7. Energy Requirement and Process Scaleup. The induction heater employed for both pyrolysis and upgrading had a maximum power input of 5 kW. To maintain the catalyst bed temperatures of 290, 330, and 370 °C, the total power

Table 5. Energy Balance for Induction Heating Applied to Biomass Pyrolysis and Upgrading

	290 °C (Run 1)	290 °C (Run 2)	330 °C (Run 1)	330 °C (Run 2)	370 °C (Run 1)	370 °C (Run 2)
E_b[a] (kJ/h)	5916	11421	4079	8606	6515	10567
E_c[b] (kJ/h)	3190	3213	3055	3099	2920	3103
E_g[c] (kJ/h)	2193	1783	1076	1543	2439	1476
E_T[d] (kJ/h)	11299	16417	8210	13249	11874	15416
$E_{\text{Induction}}$[e] (kJ/h)						
biomass heating	4320	4320	4320	4320	4320	4320
catalyst heating	1440	1440	1800	1800	2520	2520
total $E_{\text{induction}}$[f]	5760	5760	6120	6120	6840	6840
E_{bal}[g] (kJ/h)	5540	10658	2090	7129	5035	8308
heat loss (kJ/h)						
reaction tube	3261.1	3261.1	3261.1	3261.1	3261.1	3261.1
catalyst tube	580.5	580.1	638.55	638.55	774.0	774.0
estimated E_{ind}[h]	3070.88	3070.88	3390.24	3390.24	4015.43	4015.43
E_{ratio}[i]	1.96	2.85	1.34	2.16	1.73	2.21
estimated E_{ratio}	3.67	5.34	2.42	3.90	2.95	3.77

[a] Energy in bio-oil obtained from pyrolysis after upgrading. [b] Energy in char obtained from pyrolysis after upgrading. [c] Energy in gas obtained from pyrolysis after upgrading. [d] Total output energy. [e] Electrical energy consumed by induction heater for biomass and catalyst heating individually. [f] Electrical energy consumed during pyrolysis and upgrading. [g] Energy balance defined as output energy − energy consumed. [h] Estimated electrical energy consumed during pyrolysis and upgrading after controlling 70% of heat losses. [i] Energy ratio defined as the energy content of the products divided by the electrical energy consumed.

inputs for the heater were 8%, 10%, and 14%, respectively, corresponding to 400, 500, and 700 W, respectively. The total energy input for biomass pyrolysis at 600 °C was 24% of 5 kW, corresponding to 1200 W. Induction heating generally has a high efficiency of ~85%, compared to other heating techniques, as only 15% of the energy is lost as heat energy to the surroundings,[20,30] but these values are listed for insulated systems, which was not the case in these experiments. The associated convective and radiative heat losses are estimated in the following paragraphs. In any case, as indicated by the results above, the power requirement for induction heating is also high (Table 5). We determined the high heating value (HHV) of the char, gas and liquid samples to calculate the energy recovery of the overall process, including upgrading.

The radiative and convective heat losses for reaction and catalyst tube was calculated from the following equation:

$$P = \varepsilon \sigma A[T_t^4 - T_t^4] + hA[T_t - T_\infty]$$

where P is the total power (W), ε the emissivity of the reaction tube (measured as 0.76), σ the Stefan−Boltzmann constant (56.7×10^{-9} W/m^2 K^4), T_t the tube temperature, T_a the ambient/room temperature, A the area of the reaction tube, and h the convective heat-transfer coefficient (28 W/m^2 K). The first term on the right-hand side of the equation represents the radiative heat transfer and the second term is the convective heat transfer. By using insulation to control 70% of these heat losses, the actual energy input is reduced and an overall energy ratio of ≥3.0 is obtained for all operating temperatures, with the highest overall energy ratio being obtained at the lowest temperature of 290 °C. This energy ratio is sufficient to operate a generator with a thermal efficiency of 33%, which indicates the feasibility of using this approach. In the present study, much of the energy inputs into both the pyrolysis and upgrading systems are coming from the startup of the induction systems. As the system is scaled up and converted to a continuous system, these energy costs can be lowered, with a corresponding increase in overall efficiency.

In other studies, Fuji Electric Company has demonstrated pyrolysis with an induction heater without catalytic upgrading.[20] The feed rate for their study was 100 kg/h, with an electrical power input of 100 kW/h.[20] The total output energy of 1940 MJ/h was achieved, distributed as 750, 640, and 550 MJ/h for oil, char, and gas, respectively. The power input for the process was 360 MJ/h, corresponding to 18% of the total energy output, demonstrating good efficiencies at higher scales. The experimental setup presented herein was not optimized for efficiency but for higher yield, with its main objective being to demonstrate that catalytic upgrading can be carried out using a fast and relatively easy induction heating method, with better results for catalyst upgrading, compared to conventional heating. Further studies to optimize the process and increase the efficiency are required and will be reported in further studies.

Scaleup of induction-heating-based processes for different applications have been attempted in the past. For example, Fuji Electric Company built an induction-based kiln for the continuous pyrolysis of industrial waste, mainly plastics for demonstration.[20] Since induction heating directly heats the metal and transfers heat to the biomass, heat losses associated with heating the heat carrier are eliminated. Many designs can be implemented to increase the efficiency of the process by reducing the temperature gradient. For instance, biomass can be mixed with metal balls for direct heating. Metallic fins or baffles can be inserted inside the reactor to increase temperature uniformity. The accumulation of soot does not affect the efficiency of induction heating; hence, the startup and shutdown times for induction-heating-based processes are shorter.[20,30]

4. CONCLUSION

Pyrolysis of biomass and catalytic upgrading was performed using induction-heating technology. Different process parameters were tested. The results were compared to those of conventionally heated catalysts. As the temperature and C/B ratio each increase, the quality of oil increases and a higher aromatics yield is obtained with the inductively heated catalyst. Lower coke deposition, higher BET surface area, and acid site intensity is observed for the inductively heated catalyst, compared to conventional heating. This study demonstrates the use of induction heating for pyrolysis and vapor upgrading of biomass for the production of higher-grade bio-oil and notes the design simplicity and ease of operation, as well as enhanced performance, compared to conventional heating methods. This technique shows a promising pathway for catalyst and biomass heating and should be further investigated for development and large-scale operations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b01878.

> Comparison of properties, in terms of yield, water content, and elemental analysis of bio-oil obtained from conventional and inductive upgrading techniques (the catalyst temperature was maintained at 290°, 330° and 370 °C and the catalyst-to-biomass (C/B) ratio was 2) (PDF)

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Notes

The authors declare no competing financial interest.

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