SYNTHESIS AND EVALUATION OF NOVEL BIOCHAR-BASED AND METAL OXIDE-BASED CATALYSTS FOR REMOVAL OF MODEL TAR (TOLUENE), NH_3, AND H_2S FROM SIMULATED PRODUCER GAS

By

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Abstract: Gasification is a thermochemical conversion process in which carbonaceous feedstock is gasified in a controlled atmosphere to generate producer gas. The producer gas is used for production of heat, power, fuels and chemicals. Various contaminants such as tars, NH_3, and H_2S in producer gas possess many problems due to their corrosive nature and their ability to clog and deactivate catalysts. In this study, several catalysts were synthesized, characterized, and tested for removal of three contaminants (toluene (model tar), NH_3, and H_2S) from the biomass-generated producer gas. Biochar, a catalyst, was generated from gasification of switchgrass. Activated carbon and acidic surface activated carbon were synthesized using ultrasonication method from biochar. Acidic surface was synthesized by coating activated carbon with dilute acid. Mixed metal oxide catalysts were synthesized from hydrotalcite precursors using novel synthesis technique using microwave and ultrasonication.

Surface area of activated carbon (~900 m^2/g) was significantly higher than that of its precursor biochar (~60 m^2/g). Surface area of metal oxide catalyst was approximately 180 m^2/g after calcination. Biochar, activated carbon, and acidic surface activated carbon showed toluene removal efficiencies of approximately 78, 88, and 88 %, respectively, when the catalysts were tested individually with toluene in the presence of producer gas at 800 °C. The toluene removal efficiencies increased to 86, 91, and 97 % using biochar, activated carbon and acidic surface activated carbon, respectively in the presence of NH_3 and H_2S in the producer gas. Increase in toluene removal efficiencies in presence of NH_3 and H_2S indicates that NH_3 and H_2S play a role in toluene reforming reactions during simultaneous removal of contaminants. Toluene removal efficiency for mixed metal oxide was approximately 83%. Ammonia adsorption capacities were 0.008 g NH_3/g catalyst for biochar and 0.03g NH_3/g catalyst for activated carbon, acidic surface activated carbon, and mixed metal oxide catalyst. H_2S adsorption capacities were 0.008 g H_2S/g catalyst for all biochar-based catalysts and 0.01g H_2S/g catalyst for mixed metal oxide. Thus, ultrasonication and microwave technology offer improved benefits for synthesis of high-performance catalysts intended for use in biomass-generated producer gas upgrading. High surface area biochar-based and metal-oxide based catalysts have high efficiencies for simultaneous removal of toluene, NH_3, and H_2S.

THESIS FORMAT

This thesis is a compilation of four chapters. The first chapter is an introduction to the scope of the thesis. Each of the remaining three chapters is written as a journal article that has either been published, is in the process of being published or is intended for publication.

The first chapter is an introduction to the scope of the thesis and an overview of objectives. Second chapter of the thesis is a review paper which covers the state-of-the-art of using carbon based catalysts for removal of producer gas contaminants. The third chapter includes synthesis and evaluation of biochar-based catalysts for removal of toluene (model tar) from biomass-generated producer gas. This is followed by the fourth chapter, where an extensive study was conducted for simultaneous removal of selected contaminants, i.e. toluene (model tar), ammonia, and hydrogen sulfide, using four novel catalysts, i.e. biochar, activated carbon, acidic surface activated carbon, and mixed-metal oxide.

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CHAPTER I

INTRODUCTION

Gasification is a thermochemical conversion process in which carbonaceous materials such as natural gas, naphtha, residual oil, petroleum coke, coal and biomass, react with a gasification medium (such as air, oxygen and/or steam) at high temperatures (600 °C-1000 °C) to produce a mixture of gases called producer gas. The major components of producer gas are carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), and hydrogen (H_2), but it also contains methane (CH_4), water, some high molecular weight hydrocarbons such as ethylene, various inorganic and organic contaminants like char, ash, tar, ammonia (NH_3), hydrogen sulfide (H_2S) sulfur dioxide (SO_2), and nitrogen dioxide (NO_2). The impurities in producer gas cause serious problems with downstream applications of the gas such as clogging the process lines, deactivating catalysts, and acting as precursors for toxic emissions.

Various physical and chemical techniques such as scrubbers and electrostatic precipitators are effective in reducing the levels of contaminants from the producer gas. However, these techniques also result in reducing the gas energy content since they are cold treatment techniques. Catalysts offer an effective approach to removal of contaminants while improving gas composition.

Carbon catalysts are unique and versatile materials having major industrial significance. The types and properties of these carbon materials are vast. Biochar is produced during biomass gasification and studies have shown that the low-cost biochar is a potential catalyst for tar removal. The surface area of biochar varies from 5 m^2/g to around 65 m^2/g depending on the type of biomass and gasification operating conditions. Effectiveness of the biochar to remove tar can be drastically increased by increasing its surface area and improving its chemical properties. Several studies suggest that increasing surface area of catalyst is critical to efficient tar removal using biochar. Activated carbon is a highly porous material with high surface area. Generally, activated carbon can be synthesized by either chemical activation, physical activation, or a combination of chemical and physical activation of a carbon precursor, such as biochar. In the study carried out in chapter I, selected biochar-based catalysts have been evaluated for their efficiency to remove contaminants from simulated biomass-derived producer gas. It was hypothesized that use of ultrasonication during synthesis step of the catalysts helps improve catalyst surface area, and thus improve contaminant removal efficiency.

A promising group of chemicals, hydrotalcites, are used for adsorption and separation processes and as stabilizers and catalysts. Hydrotalcites can act as precursors to mixed metal oxides, which have shown promise for removal of sulfur containing compounds. The conventional synthesis technique for hydrotalcites is expensive, requires a long time for crystallization, and requires high temperature and pressure conditions. In this study, use of microwave and ultrasound technology for synthesis of hydrotalcites is hypothesized to decrease crystallization time and generate high surface area hydrotalcites.

Simultaneous removal of various contaminants is of prime importance since it offers cost-saving benefits due to lesser unit operations and stages involved in the process. Carbon-based catalysts have several advantages for simultaneous removal of contaminants as they have been proven to be effective for individually removing tars, ammonia, H_2S, and CO_2 as discussed previously.

Also, mixed metal oxides have potential as catalysts for removal of tar. Very little literature is available attempting simultaneous removal of contaminants as there are numerous challenges involved. The focus of the third part of this study (chapter IV) was simultaneous removal of contaminants using biochar-based and metal oxide based catalysts. Both the sets of catalysts, i.e. biochar-based and metal oxide-based catalysts, were synthesized using novel techniques utilizing microwave and ultrasound technology.

Overall, an improved system and method is provided for catalytically upgrading biomass-generated producer gas in this study. One aspect of this study focused on the synthesis of two sets of catalysts, i.e. biochar-based and metal-oxide based catalysts. Another aspect of the present study focused on evaluating these synthesized catalysts (biochar, activated carbon, acidic surface activated carbon, and mixed metal oxide) for removal of tars, ammonia, and H_2S from biomass-generated producer gas. The specific objectives were to:

1. review selected carbon-based catalysts such as char, activated carbon, carbon fibers and carbon molecular sieves, for removal of various contaminants such as ammonia, hydrogen sulfide, tars, and carbon dioxide in producer gas obtained from biomass gasification,
2. synthesize activated carbon from switchgrass gasification-based biochar precursors and evaluate the effect of ultrasonic potassium hydroxide (KOH) impregnation on the properties of the activated carbon,
3. evaluate the effectiveness of biochar, activated carbon and acidic surface activated carbon on removal of toluene as a model tar,
4. examine a novel technique for synthesis of fourth catalyst i.e. mixed metal oxide, using microwave and ultrasound, and

5. evaluate effectiveness of the four synthesized catalysts (biochar, activated carbon, acidic surface activated carbon, and mixed metal oxide) for simultaneous removal of toluene (model tar), ammonia, and H_2S in fixed-bed reactor experiments.

CHAPTER II

REVIEW ON USING CARBON-BASED CATALYSTS FOR PRODUCER GAS CONTAMINANTS REMOVAL

Abstract

Gasification is a thermochemical conversion process in which carbonaceous feedstock is gasified in a controlled atmosphere to generate producer gas, consisting primarily of CO_2, CO, H_2, and CH_4. CO and H_2 are the most desirable constituents, used in downstream applications such as combustion to generate heat and power or conversion into fuels and chemicals. CO_2 is a greenhouse gas which is increasingly being regulated due to its negative impact on the environment. Also, since CO_2 is in its completely oxidized state, it does not have any heating value. Apart from these gases, the producer gas also consists of tars, NH_3, and H_2S which possess various problems due to their corrosive nature and their ability to clog and deactivate catalysts. These contaminants must be removed to improve the gas quality before the gas is usable in downstream applications. Carbon-based catalysts include a wide variety of catalyst types such as activated carbon, char and molecular sieves. These catalysts are increasingly being used in various gas cleaning and upgrading applications due to their wide variations in properties such as conversion efficiency, selectivity, mechanical strength, ease of synthesis, sustainable precursors and cost. This paper will review these carbon-based catalysts, their synthesis techniques and properties, and their applications for producer gas cleanup.

Keywords. Producer gas contaminants, tar, ammonia, H_2S, carbon-based catalysts

1 Introduction

Gasification is a thermochemical conversion process in which carbonaceous materials (such as natural gas, naphtha, residual oil, petroleum coke, coal and biomass) react with a gasification medium (such as air, oxygen and/or steam) at high temperatures (600 to 1000 °C) to produce a mixture of gases called producer gas [1-4]. The major components of producer gas are carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), and hydrogen (H_2), but it also contains methane (CH_4), water, some high molecular weight hydrocarbons such as ethylene, various inorganic and organic contaminants like char, ash, tar, ammonia (NH_3), hydrogen sulfide (H_2S) sulfur dioxide (SO_2), and nitrogen dioxide (NO_2) [3, 5-9]. The impurities in producer gas can cause serious problems with downstream applications of the gas such as clogging the process lines, deactivating catalysts, and acting as precursors for toxic emissions [10-13].

Tar can be defined as all organic contaminants having molecular weights higher than benzene [14]. Tar content (wet basis) from biomass gasification can be as low as 4 $g \cdot N^{-1} \cdot m^{-3}$ [15] and as high as 48 $g \cdot N^{-1} \cdot m^{-3}$ [16] depending upon the type of gasifier. Tar causes problems such as clogging of fuel process lines, deactivating catalysts, and disrupt engine and turbine functioning [10, 11, 17]. Various physical and chemical removal techniques like scrubbers and electrostatic precipitators are effective in reducing the levels of tars from a gas [11, 18-20].

Ammonia (NH_3) is formed primarily from the nitrogen containing compounds present in the biomass feedstocks. This fuel bound nitrogen is released at high temperatures inside the gasifier. Ammonia is a precursor for NO_x emissions in downstream applications of the producer gas such as turbines, gas engines, and burners. NH_3 and other nitrogen containing compounds are also undesirable for catalytic upgrading and conversions as they are poisonous to catalysts. The ammonia content in producer gas can vary between 0.01 to 3 % v/v [21].

Sulfur in biomass feedstocks usually leads to the formation of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and other gaseous sulfur compounds. These sulfur compounds are toxic and can pose various problems such as catalyst deactivation, acid rain precursors, and pollution. These sulfur contaminants must be removed before the producer can be used further in turbines or fuel cells [13].

Various physical and chemical removal techniques such as scrubbers and electrostatic precipitators are effective in reducing the levels of contaminants from the producer gas. However, these techniques also result in reducing the gas energy content since they are cold treatment techniques. Also, the disposal of the solvents used, as well as the high costs of the equipment and operation, makes scrubbing inefficient and uneconomical. Catalysts offer a more cost efficient and equally effective approach to removal of contaminants [18]. Carbon catalysts are unique and versatile materials having major industrial significance [22]. Carbon catalysts find utility in many real-world applications such as energy storage, energy conversion, sensors, and contaminants removal. Carbon catalysts can be synthesized either through gas phase, solid phase, or liquid phase reactions from precursor materials containing carbon. Hydrocarbons are the most widely used precursors for synthesis of carbon catalysts. Properties of carbon catalysts relate directly to their structure. The catalyst structure in turn relates to the carbon precursors used for their synthesis. The various types of carbon catalysts are graphite, pyrolytic carbon, carbon fibers, glasslike fibers, activated carbon, carbon blacks, coke, and char [23].

This paper reviews selected carbon-based catalysts such as char, activated carbon, carbon fibers and carbon molecular sieves, for removal of various contaminants such as ammonia, hydrogen sulfide, tars, and CO_2 in producer gas obtained from biomass gasification. The various carbon-based catalysts are reviewed according to their chemical and physical composition, their precursors and synthesis techniques, and properties. This discussion is followed by a review of published results on effectiveness of catalysts for removal of contaminants. Finally, recommendations are made based on conclusions derived from the review.

2 Carbon catalysts

The atomic number of carbon is 6 and its electronic configuration is $1s^2$, $2s^2$, $2p^2$. In the solid form, carbon exhibits three types of structures i.e. tetrahedral diamond structure, hexagonal graphite, and linear carbynes. These structures correspond to hybridization states of sp^3, sp^2, and sp^1, respectively. Carbon materials in multicomponent systems are called “carbon alloys” [24]. Graphite carbon in sp^2 state of hybridization can be classified into graphitic and non-graphitic carbon; whereas non-graphitic carbon can be further classified into graphitizable and non-graphitizable carbon [25]. Graphitic carbon consists of graphenes arranged parallel to each other in a tridimensional crystalline network. Coke, pyrolytic carbon, carbonaceous mesophase, pitch, and carbon fibers are all graphitizable. Non-graphtizable carbons include char, activated carbon, wood charcoal, and some types of coal. The various categories into which the pores on carbon adsorbents can be classified are given in Table 1. Each of the three types of pores i.e. micropores, mesopores, and macropores, play a role in the adsorption process. Macropores act as openings and channels for the adsorbate molecules to quickly enter inside the catalyst. Micropores are filled with adsorbate gas at low vapor pressure and are volume filled as compared to capillary condensation [26]. Mesopores, fill at relatively high vapor pressures and through capillary condensation mechanism [23].

Table 1: General characteristics of various types of porosities in carbon adsorbents.

Type of porosity	Pore radii (nm)	Pore volume ($m^3 \cdot kg^{-1}$)	Function in adsorption
Micropore	<2	0.00015-0.0007	Volume filling
Mesopore	2-50	0.0002-0.00065	Filled through capillary condensation
Macropore	50- 2000	0.0002-0.0004	Channel for adsorbate

to reach inside particle

2.1 Char

Char is a non-graphitizable material and is defined as a product of a carbonization process of carbonaceous precursors without achieving a fluid state in the process [23, 27]. Incomplete combustion or thermochemical treatment of a carbonaceous precursor gives rise to a black solid material rich in carbon content known as char. Char can be derived from coal or biomass. Char derived from biomass is popularly known as biochar. If derived from wood, it is known as wood-char. If derived from coal it is known as charcoal or coal-char. Various thermochemical processes such as gasification, pyrolysis, and combustion give rise to char which is mostly considered a waste material. However, being rich in carbon, char is in some instances being used as a source of fuel. Char also shows promise as an organic fertilizer [28].

Char can be synthesized from a variety of feedstocks. Biochar can be synthesized from perennial grasses, switchgrass [29], miscanthus [30], forestry waste, crop residues, animal manure, sewage, and waste. Wood char can be obtained from pinewood [31], maple [32], birch [33], and poplar [34]. Coal char can be derived from either peat [35], lignite [36], bituminous [37], or anthracite [38] types of coal.

The synthesis process for making chars can either be called carbonization, charring, devolatilization, or pyrolysis. Thermal decomposition of biomass or coal in low oxygen environments volatilizes the precursor and gives rise to char. Traditional charcoal manufacturing occurs in pits or kilns; whereas modern systems employ large-scale and continuous pyrolyzers. Pyrolysis occurs in the absence of oxygen while gasification is a partial oxidation process. The gas, solid, and liquid yields differ according to the process types or process conditions used [5]. Table 2 gives a summary of the process conditions and the product distribution for various types of char synthesis processes. It shows that pyrolysis results in a higher char yield compared to gasification. Also, slow pyrolysis favors the formation of char; whereas, fast pyrolysis favors higher liquid yield. The exact mechanism for char formation differs by process to process; however the basic pathway followed can be summarized as follows. During biomass or coal heating, there is a decrease in mass due to formation of volatile organics. A mineral and carbon skeletal structure is formed primarily due to carbonization of the precursor which creates the porous char structure [5, 27].

Table 2: Pyrolysis and gasification properties and product distribution (adapted from Bridgwater [23])

Technology	Temperature (°C)	Residence Time (s)	Char (%)	Liquid (%)	Gas (%)
Fast pyrolysis	~500	~1	12	75	13
Medium pyrolysis	~500	10 to 20	20	50	30
Slow pyrolysis	~500	~300 to 1800	35	30	35
Gasification	>750	~10 to 20	10	5	85

As part of the discussion on the physical properties of char, the properties significant to the catalytic performance (Table 3) should be addressed. Surface area of the char has a significant effect on adsorptive capacities. The surface area of biochar varies from less than 1 $m^2 \cdot g^{-1}$ [39] to 100 $m^2 \cdot g^{-1}$ [27]. Fig. 1 shows porosities and surface characteristics of a sample of biochar. The average pore volume of biochar can be as high as 1.2×10^{-6} $m^3 \cdot g^{-1}$ [40] and as low as 2×10^{-8} $m^3 \cdot g^{-1}$ [41, 42]. Average pore diameters of biochar can range from 3 to 300 nm [40, 41]. Particle density of char derived from switchgrass, corn stover or hardwood ranges from 1.5×10^6 to 2×10^6 $g \cdot m^{-3}$ [27]. Biochar has high silica ash content which might present challenges to traditional char applications such as tar removal or activation [27, 43].

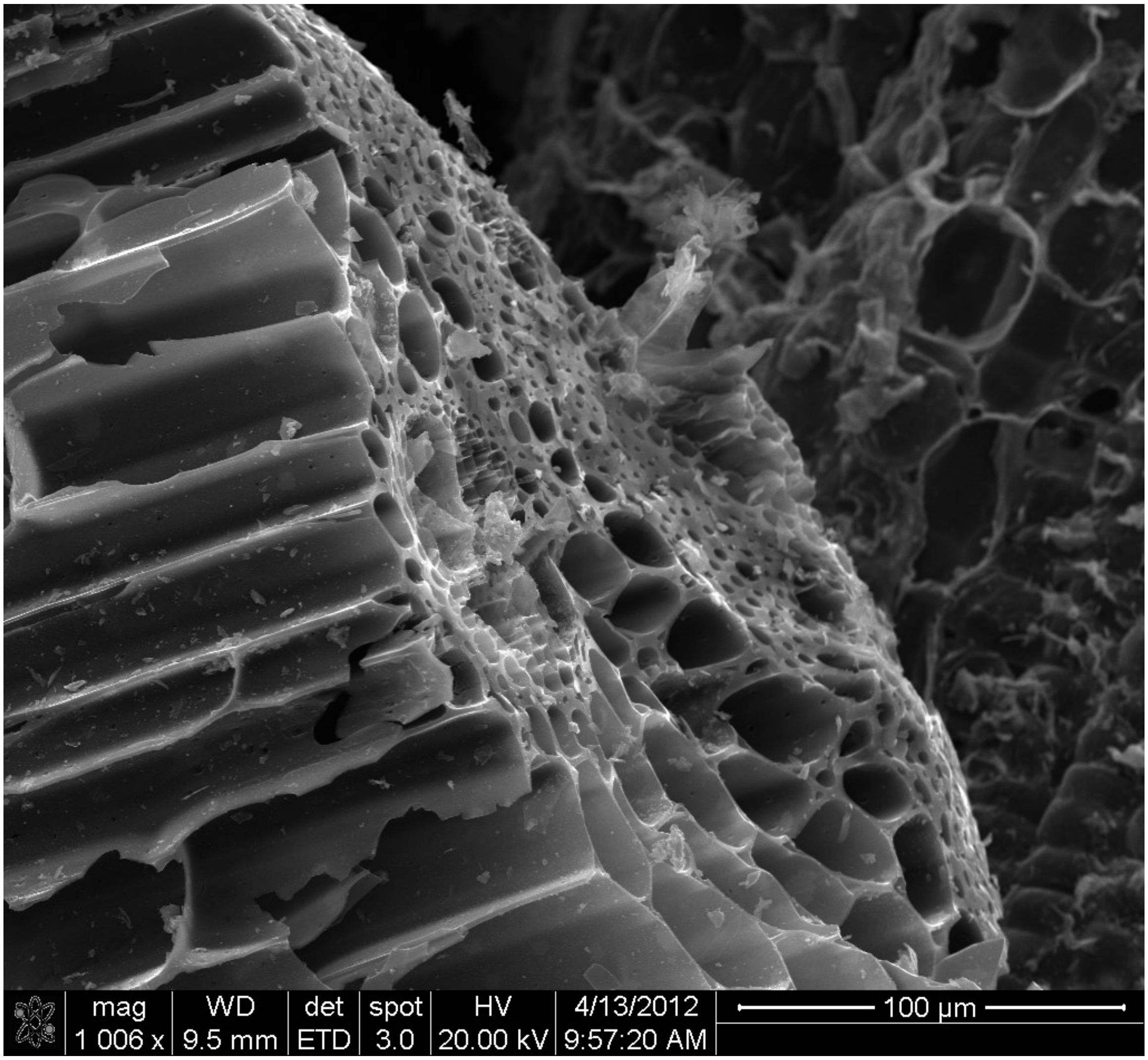

Fig.1. Scanning electron microscopy image of gasifier-derived biochar showing pore openings

2.2 Activated carbon

Activated carbon is a highly porous material [26]. Surface area, pore diameter, and pore volume of activated carbon range from 100 to 3000 $m^2 \cdot g^{-1}$ [44], 1.9 to 3.5 nm [45], and 5×10^{-7} to 9×10^{-7} $m^3 \cdot g^{-1}$ [43], respectively (Table 3). Generally, activated carbon is synthesized by either chemical activation, physical activation, or a combination of chemical and physical activation of a carbon precursor [46, 47]. This activation process gives rise to a highly porous carbon material showing adsorptive properties higher than those for the original precursor. The carbon precursor can be any material with carbon as its primary constituent. Various agricultural residues such as wheat [48], rice husks [49], sugarcane bagasse [49], corn stover [50], hazelnut [51], and biomass-based biochar [46] have been used to synthesize this activated carbon. The activated carbon can be processed in either granular [52], powdered [26], fibrous [53], or cloth [54] form. Large internal surface area and small pores are the characteristics of granular activated carbon. Powdered forms have large pore diameters and small internal surface areas. Large surface area and wide pores are the characteristics of activated carbon cloth and fibers [26].

Fig. 2 shows porosities developed in activated carbon derived from gasifier biochar. Depending on the synthesis technique, activated carbon shows either microporous or mesoporous structure can be developed. Popular techniques for the synthesis of microporous carbons are pyrolysis of carbon precursors [55] and carbon deposition on a zeolitic surface [56]. Mesoporous carbons are commonly synthesized using metal ions [57] or silica templates [58]. The interlayer spacing of graphite is 0.335 nm; whereas, activated carbon interlayer spacing is between 0.34 nm and 0.35 nm [53]. Activation process causes an increase in pore diameter as well as pore volume. The carbonization process gives rise to a porous structure. The burning process during carbonization called ‘burnoff’ causes a decrease in the disorganized carbon matter, volatile matter, and walls between the adjacent pores. When this degree of burnoff is less than 50 %, it causes development of microporous carbon. Greater than 75 % burnoff produces macroporous carbon. Burnoff of 50 % to 75 % causes a formation of a mixed porous structure [59].

Chemical structure of the activated carbon strongly influences its adsorption capacities. Van der Waals forces of attraction play a decisive role in the adsorption process. Also, the presence of burned graphite layers due to the carbonization process creates unpaired electrons in the carbon skeleton, effecting the adsorption of polar and polarizable compounds [26].

Acid-base character of carbon is formed as a result of surface oxidation of the carbon. When carbon is treated with oxygen at temperatures up to 400 °C, formation of acidic surface groups on the carbon occurs. The acidic groups give a hydrophilic and polar characteristic to the surface [60]. Basic surface oxygen groups are formed when an oxygen-free carbon surface, after heat treatment at 1000 °C in an inert atmosphere, is in contact with oxygen [61]. Irreversible chemisorption of oxygen at unsaturated sites on the carbon surface gives rise to neutral surface activated carbons [61].

The main adsorbing surfaces of activated carbons are aromatic sheets present on its outer periphery. Various modification techniques depending upon the type of application are used to form surface groups such as carbon-hydrogen, carbon-nitrogen, and carbon-sulfur. This ability to modify the surface groups of the activated carbon is one of its most important properties [26]. Some of the more common surface modification techniques are nitrogenation [62, 63], halogenation [64], sulfurization [65, 66], and impregnation [47, 67].

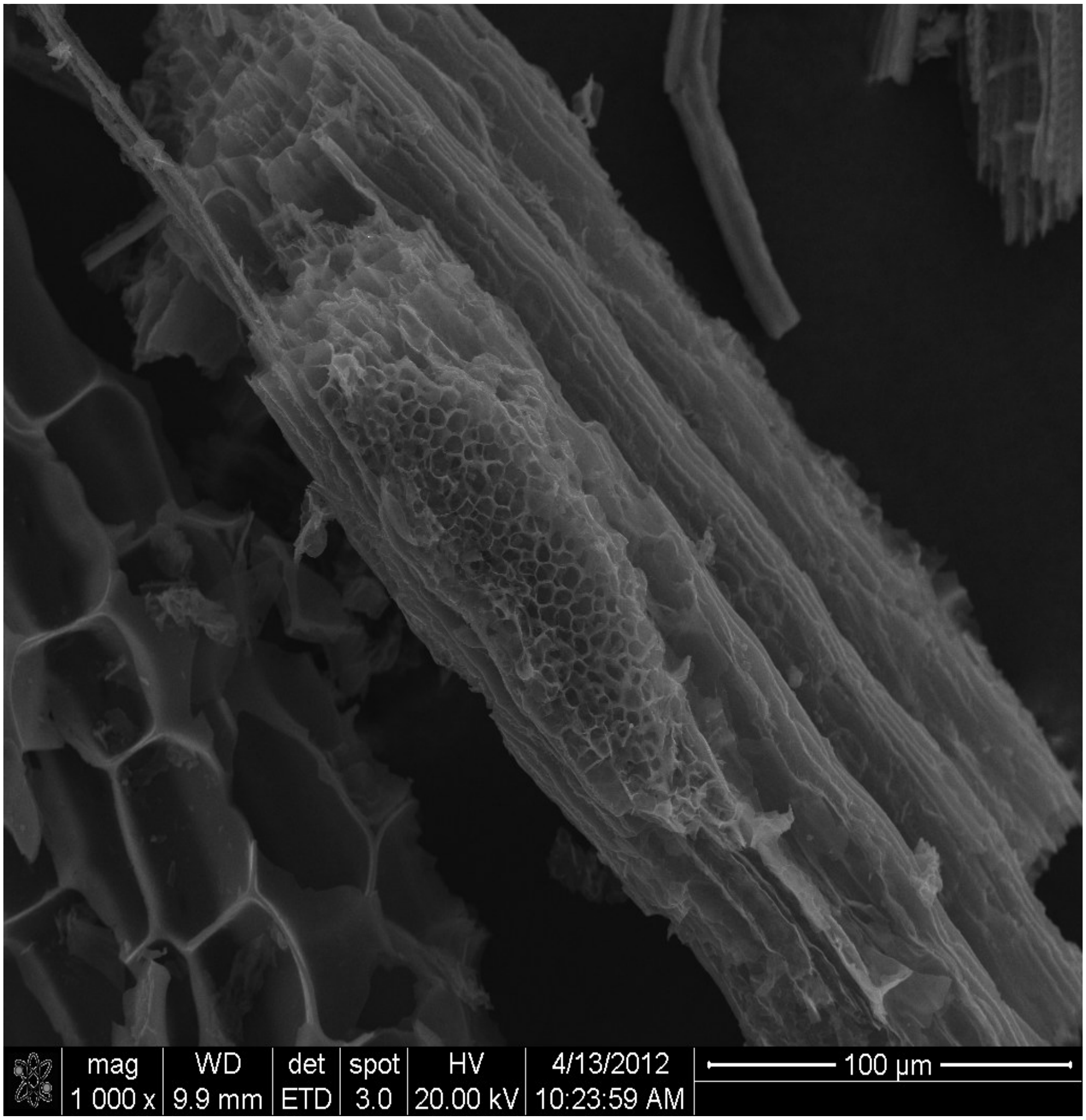

Fig.2. Scanning electron microscopy image of activated carbon showing large pore openings.

2.3 Carbon fibers and derived cloths

Carbon fibers or activated carbon fibers (ACF) and derived cloths are carbon-based materials which have a uniform pore size distribution and a small uniform fiber diameter [53, 68]. Due to this structure, these materials have size selectivity for the adsorbate as well as fast sorption kinetics as compared to pelletized or granular activated carbons [53]. The primary advantage of using carbon fibers over granular activated carbons is that their thin fibrous shape provides faster intraparticle adsorption. Intraparticle diffusion resistance is higher in granular activated carbons resulting in reduced adsorption capacity of the catalyst and thus a larger size of adsorption unit must be used [53]. ACFs are generally synthesized from nongraphitizable fibrous precursors such as coal tar pitch, phenol-formaldehyde fibers, viscous textiles and polymers [69-71]. The synthesis process involves spinning the precursors such as coal tar pitch and polymer into a fiber shape followed by carbonization and activation of the fibers. These carbon fibers have a small diameter (10 µm to 40 µm) and hence have a higher packing density which is beneficial to gas storage type applications [72, 73]. The pore size distribution is essentially microporous. These materials have fast sorption kinetics (as high as 130 $g \cdot mg^{-1} \cdot h^{-1}$) [74, 75] due to lack of mass transfer limitations. The adsorption process on carbon fibers usually proceeds via volume filling rather than surface coverage [23].

2.4 Carbon molecular sieves

Carbon molecular sieves (CMS) are porous carbons having narrow pore size openings around 3 nm diameter [58] and are usually synthesized usually using carbon vapor deposition (CVD) of hydrocarbons. A variety of processes such as CVD and carbonization exist for synthesis of carbon molecular sieves. Most of the processes involve thermal decomposition of gaseous hydrocarbon in a furnace at high temperature (600 to 1000 °C) depositing the decomposed product onto a carbonaceous surface [76]. Popular synthesis techniques reported synthesis carbon molecular sieves by carbonization of substances such as polyvinylidene chloride resin [77], phenol or furan resin [78], and sulfite pulp [79]. CVD causes carbon to deposit on the pore entrances. CMS materials are used for capturing very small molecular compounds. Carbon molecular sieves exhibit hydrophobicity [23, 26, 53]. Carbon molecular sieves can be synthesized with surface areas ranging from 1300 $m^2 \cdot g^{-1}$ [58] to around 3600 $m^2 \cdot g^{-1}$ [80]. There is almost no mesoporosity in its structure [80]. Molecular structure of carbon molecular sieves consists of a condensed aromatic ring system [80].

Table 3: Surface characteristics of catalysts

Catalyst	Pore Diameter (nm)	Pore Volume ($m^3 \cdot kg^{-1}$)	Surface Area ($m^2 \cdot g^{-1}$)	Reference
Biochar	3-300	0.02×10^{-5}-1.2×10^{-3}	<1 $m^2 \cdot g^{-1}$ to 100 $m^2 \cdot g^{-1}$	[26, 38, 39, 40, 41, 42]
Activated Carbon	1.9-300	0.5×10^{-3}-0.9×10^{-3}	100-3000	[42, 43, 44]
Carbon fibers	0.7-2	1×10^{-3}	3000	[1]
Carbon Molecular Sieves	3	0.3×10^{-3}-1.1×10^{-3}	1300-3600	[67, 68]

3 Effectiveness of carbon catalysts to remove producer gas contaminants

Carbon-based catalysts are being used increasingly to remove various contaminants such as ammonia, hydrogen sulfide, tars, and carbon dioxide from coal and biomass gasification gas. These carbons not only act as effective catalysts for hot-gas cleanup, but also for removal of contaminants dissolved in scrubbing solutions and solvents. Some of the applications where carbon-based catalysts have been successfully employed and evaluated include biomass and coal gasification, pyrolysis, and combustion.

3.1 Sulfur compounds

The volume fraction sulfur content in the biomass feedstocks ranges from 0.05 % for *L. leucocephala* [81] to 1.6 % for Kanlow switchgrass [82]. This sulfur is released in the form of H_2S and SO_x when the biomass is gasified or combusted [81]. The H_2S content in the producer gas usually ranges from volume fraction 0.02 % for wheat straw to 0.08% for switchgrass [83]. These sulfur-containing compounds not only have a hazardous effect on health and the environment, but also lead to deactivation of downstream catalysts.

High surface area, fast adsorption kinetics, low attrition rate, stability in reducing conditions, resistance to deactivation by other contaminants, and easy regeneration of spent catalyst are some of the desired properties of a sulfur sorbent. Activated carbon shows promise as a catalyst for sulfur adsorption. Its low cost and easy synthesis offers additional advantages. Adib et. al. [84] suggested that the choice of sulfur sorbent be made based on acidity of the sorbent and associated parameters such as number of acidic groups, surface pH, and amount of surface oxygen groups. The reaction mechanism of H_2S adsorption on the carbon surfaces can be summarized into three types of reactions:

$$C + H_2S \rightarrow CS + H_2 \tag{1}$$

$$CO + H_2S \rightarrow CS + H_2O \tag{2}$$

$$CM + H_2S \rightarrow CMS + H_2 \tag{3}$$

where, CM represents carbon metal and CMS represents carbon-metal-sulfide. Oxidation of activated carbons decreases H_2S removal capacity due to a decrease in pH of the catalyst. Thus, the activated carbon should not be stored in possible oxidizing atmosphere for long time. Adib et. al. [84] measured the H_2S breakthrough capacity on two types of activated carbons i.e. synthesized from coconut shell and from bituminous coal. Oxidation of the activated carbon significantly decreased the H_2S removal performance of the catalyst. Researchers attributed this phenomenon to a decrease in catalyst pH as a result of oxidation of the catalyst [84, 85]. They also noted that the synthesized activated carbon cannot be stored for a long time since oxidation will decrease its catalytic activity.

Producer gas components affect H_2S adsorption onto activated carbon. Cal et. al. [85] carried out a series of experiments to evaluate the adsorption of H_2S on activated carbon at high temperatures (400 to 600 °C). They found that decreasing the CO_2 concentrations in the inlet gas decreased the H_2S breakthrough time (defined as time at which outlet H_2S gas concentration reaches volume fraction of 0.02 %). This suggests that CO_2 partially gasifies carbon sites on the catalyst surface and forms C-O complexes. This interaction enhances H_2S adsorption. The addition of CO, H_2, and H_2O had a detrimental effect on H_2S adsorption. Zn and Cu impregnated activated carbons performed well for adsorption (breakthrough time of 75 minutes). Cal et. al. [86] also studied effects of high temperature (400 to 600 °C), high pressure (1 MPa), and gas composition on H_2S

adsorption by the activated carbon. Increasing the pressure from 0.1 to 1 MPa improved H_2S adsorption. However, varying the temperature from 400 to 600 °C had no effect on H_2S adsorption. For metal based sorbents, H_2S adsorption performance considerably decreases (breakthrough time decreases from 75 minutes to around 70 minutes) as the reaction temperature decreases below 500 °C. The lack of change in H_2S adsorption by the activated carbon for 400 to 600 °C temperature range are promising results since it opens the possibility of using these sorbents at gasification gas exit temperatures and thus avoiding heat losses while reducing costs. The researchers suggest that H_2 regeneration seems to be a promising technique for the carbon sorbent as up to 100 % of previously adsorbed H_2S was removed using H_2 gas [86].

Fe impregnation onto activated carbon improves its efficiency to remove sulfur compounds. Sakanishi et. al. [87] investigated the adsorption and decomposition of H_2S and COS over activated carbons derived from a brown coal at temperatures of around 400 °C. They concluded that activated carbon helps remove COS which adsorbs onto the pores of the activated carbon and reacts with the carbon surface to form CO. They also suggest that H_2S removal efficiency onto Fe-impregnated activated carbon was higher as compared to that of plain carbon since H_2S reacts with the Fe metal to produce metal sulfide. They also found that the COS failed to decompose over the Fe-impregnated sorbent. This indicates that H_2S may be preferentially and competitively adsorbed and decomposed as compared to COS over the Fe-impregnated carbon.

Microporosities and surface oxygen groups improve sulfur removal efficiency whereas surface acidic groups tend to decrease sulfur removal efficiency. Boudou et. al. [88] investigated the effect of ammonia treatment on activity of viscose-based activated carbon cloth (ACC) for the adsorption/retention of H_2S and SO_2 at room temperature in the presence of moisture. They found that the ammoxidation process (treatment with ammonia and air) decreased the porosity, surface area, and sulfur removal capacity of the carbon cloth; whereas, ammoxidation followed by carbonization of the carbon improved surface area but had no effect on sulfur removal. Further, modification of the activated carbon by ammonia and steam at 800 °C improved the sulfur removal capacity as microporosities and basic oxygen groups were developed which aided CO generation at high temperature.

Another property beneficial for sulfur removal is presence of basic sites on the catalyst surface which enhances oxidation efficiency of the catalysts. Xiao et. al. [89] evaluated the catalytic activity of activated carbons derived from coal and impregnated with Na_2CO_3 and determined that Na_2CO_3 impregnation enhances the oxidation efficiency of the catalyst. Water played a beneficial role in the adsorption process. In addition, elemental sulfur was the major product formed as a result of the oxidation process along with a small amount of H_2SO_4. The H_2SO_4 tends to deactivate the catalyst but Na_2CO_3 impregnation helps to maintain the porosity by providing a basic environment. Activated carbon fibers (ACF) were evaluated as H_2S adsorbents by Feng et. al. [90]. They found that ACFs performed well for H_2S adsorption and increasing heat treatment of the catalyst prior to use further improved its performance. Basic sites on the ACFs played a role in the adsorption process, but the sulfur compounds were strongly bonded onto the carbon which might hamper the sorbent regeneration process. Oxidation of the fibers prior to use aided the sorption process.

Presence of CO_2 also seems to enhance sulfur removal. Itaya et. al. [91] studied effectiveness of coke sorbent for H_2S adsorption. H_2S and COS were both not only adsorbed by the sorbent but also that the presence of COS and CO_2 enhanced H_2S adsorptivity. Chemical reactions involving COS and CO_2 play a role in enhancing H_2S adsorption. Also, formation of CO complexes between the microporous/mesoporous walls of the carbon surface and CO_2 helped in sulfur removal. Other techniques also exist to improve H_2S adsorption by carbon catalysts. H_2S adsorption has been proven to be enhanced by chemical alteration of the surface functionality [92], pH [93] and/or applying chemical activation using NaOH [94], KOH [95], K_2CO_3 [94, 96], Na_2CO_3 [94], H_2SO_4 [95], H_3PO_4 [97], and Zn [85, 97].

3.2 Ammonia and HCN

Ammonia gas is a key raw material in manufacturing many chemicals such as nitric acid, urea, plastics, rubbers, disinfectants, and pesticides. It is also used as a coolant, pharmaceutical raw material, and manufacture of explosives. However, it is a toxic gas and can cause severe damage to humans, animals, and the environment. Adsorption processes are being researched to develop efficient catalytic techniques for mitigating the NH_3 problem during gasification and combustion. Various sorbents are being evaluated and tested such that they can be used in these catalytic techniques.

Ammonia removal using catalysts/sorbents is thought to proceed through one of the following two reaction mechanisms [13]:

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{4}$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{5}$$

Reaction (4) is called as catalytic decomposition reaction, whereas reaction (5) is called as selective catalytic decomposition, which requires oxygen. Chemical decomposition of ammonia is not feasible since producer gas has a high concentration of H_2 (10 %–30 %) [3, 7, 8]. Recent research focused on the use of high surface area acidic sorbents to capture the ammonia rather than its decomposition [17, 18].

An increase in temperature causes a decrease in NH_3 adsorption capacity of activated carbons. Rodrigues et. al. [98] evaluated activated carbon adsorbents for the removal of NH_3. They found that NH_3 adsorbed by the sorbent increased as the amount of NH_3 in the input stream increased. Increasing temperature led to a decrease in adsorption capacity.

Oxygen and sulfur groups on activated carbon surface increase ammonia retention. Petit et. al. [99] studied the effect of surface modification of activated carbon using Al-Zr oxycations on ammonia adsorption. They found that the Al-Zirconium oxycations provided new Bronsted acid centers and thus improved the uptake of ammonia. NH_3 is weakly adsorbed onto the calcined carbon sorbent. This may indicate that sorbent regeneration will proceed much easily as compared to catalysts where ammonia is chemisorbed. They also found that not only oxygen containing groups but also sulfur containing groups on activated carbon surface increased ammonia retention [100]. Sulfonic groups on the sorbent surface reacted with ammonia to form ammonium sulfate salts which are strongly adsorbed in the adsorbent micropores. Petit et. al. [101] also found that microporous activated carbon showed improved NH_3 adsorption when it was modified with molybdenum and tungsten oxide. They attributed this to the oxides present on the surface of the sorbent. Also, the presence of water on the sorbent surface improved NH_3 adsorption.

Acidic groups on catalyst surface enhance ammonia removal. Le Leuch et. al. [102] impregnated activated carbon with Fe, CO, and Cr metal salts and further calcined them. Strong acidic groups enhanced the NH_3 sorption on the sorbent. Adsorption of NH_3 in the presence of water takes place through a water film formed inside the pores of the catalyst which generates attractive forces for ammonia. In another study carried out by Mangun et.al. [103], activated carbon fibers were oxidized with nitric and sulfuric acids which increased their adsorption capacity and breakthrough times for toluene and NH_3. It can be inferred that activated carbon with oxygen and sulfur containing groups as well as acidic groups improve removal efficiency of ammonia.

3.3 Tars

Tars are defined as compounds of producer gas having molecular weights larger than benzene. Biomass gasification tars are mainly a mixture of polycyclic aromatic compounds, alkylated aromatic compounds, and phenolic compounds. The tars from a biomass gasification system were found to consist of 25 % benzene, 15.1 % phenol, 13.6 % toluene, 5.1 % naphthalene, and 4.9 % indene by mass as its major compounds [104]. Cateni et. al. [6] found that the average atomic tar composition was $C_{7.553}H_{8.623}O_{0.368}N_{0.204}$ over the course of 100 gasification runs. This result indicates that tar from biomass gasification mostly consists of deoxygenated hydrocarbons. Average molecular weight of tar was calculated to be around 108 $g \cdot mol^{-1}$. Benzene, toluene and phenol accounted for 60 % out of the first 10 main compounds of tar from switchgrass gasification. These 10 major compounds constitute 75 % of the total mass of tar. In a study by Pindoria et. al. [105], coal gasification tars were found to consist of highly condensed aromatic ring systems having a carbon aromaticity greater than 94 %. The aromatic structures were extensively dealkylated and only a small amount of oxygenates were detected [105]. The oxygen content by mass in tars has been found to be about 39 % [106].

Char is a non-metallic material naturally produced in gasifiers and pyrolyzers and show catalytic activity for tar destruction [17, 107-110]. Chars show catalytic reactivity mainly due to its pore size, surface area, and ash or mineral content. Char usually has an ash content of about 17 % or higher [111] and the elemental composition reveals that it contains several metals and inorganics such as phosphorus, potassium, magnesium, and others which might aid adsorption and catalytic activities.

In a downdraft gasifier, the producer gas flows through a hot bed of char as both the fuel and gases flow in a downward direction in a co-current fashion. A producer gas tar content of 48 $g \cdot N^{-1} \cdot m^{-3}$ was obtained from downdraft gasification of switchgrass [16]. Tar content in downdraft gasification is generally lower than updraft gasification as partial cracking of tar occurs in the char bed to give a lower tar content [112]. Dogru et. al. highlighted the activity of char for lower tar contents in a downdraft gasifier system [113]. Zanzi et. al. [114] found high tar removal efficiency when the gasifier product gas was passed through a partial oxidation zone followed by a bed of char. Hence, char as an in-bed catalyst also offers an interesting option for producer gas tar removal. Brandt et. al. [115] carried out a study on a gasifier where the gases are contacted with a charcoal bed. A high tar reduction of the aromatic hydrocarbons, including PAH were obtained using the charcoal bed down to 15 $mg \cdot N^{-1} \cdot m^{-3}$ tar content. Donnot et. al. [116] found that the residence time for efficient tar removal is inversely proportional to char surface area. They also investigated the carbon deposition phenomena on the char catalyst and found that at temperatures below 750 °C, a decrease in activity occurs after a short time due to coking.

Biomass char tar removal efficiencies are comparable to those of commercial catalysts. El-Rub et. al. [117] compared biomass chars to other catalysts such as dolomite, olivine, nickel, FCC catalysts, and ash using model tar compounds phenol and naphthalene in a fixed bed reactor. Biomass char performed satisfactorily for naphthalene conversion among the low-cost catalysts. In a review of tar removal catalysts carried out by the same researchers, it was concluded that char has high potential of being a low-cost and efficient tar removal catalyst [1]. Chembukulam et. al. [118] have reported complete decomposition of tar and pyroligneous liquor into gas of low calorific value over semicoke and charcoal from teakwood sawdust at 950 °C. Seshadri and Shamsi [119] reported tar cracking over a char-dolomite mixture. At high pressure (1.7 MPa), conversion of the tar was higher as compared to conversion at 0.1 MPa pressure due to secondary reactions of the tar in the pores of the sorbent material. Increase in temperature from 535 to 560 °C resulted in an increase in tar conversion rates from 15 to 25 %.

Activated carbon also seems promising as a tar removal catalyst. Griffiths et. al. [120] evaluated activated carbon for tar removal. Below 700 °C, the reduction in tar was basically due to tar retention in the carbon pores. Aromatic compounds formed deposits on the catalyst surface, whereas alkyl benzene passed considerably quicker through the bed. Various studies have been carried out evaluating the effectiveness of activated carbon for removal of various VOC compounds such as toluene [121, 122], naphthalene [123], aldehydes [124], benzene [125], anthracene [123], and others [126, 127]. Much information about the behavior of single compounds on activated carbon can be derived from these studies and applied towards development of an effective activated carbon adsorbent for gasification/pyrolysis tars.

Activated carbon decomposes tars at relatively lower levels of temperatures. Hu et. al. [128] evaluated tar removal using phenol, o-cresol, naphthalene, and 1-methylnapthalene as tar model compounds and commercial activated carbons as sorbents. They found that tar model compounds which have methyl groups were removed more effectively than those without methyl groups such as phenol and naphthalene. The adsorption capacity values obtained for tar per 100 g activated carbon were roughly 10 to 33 g. They concluded that the use of activated carbon reduced the temperature at which tar decomposed.

3.4 CO_2

The Energy Information Administration's (EIA) Annual Energy Outlook 2011 (AEO2011) report [129] projects that, in the case of no regulations being enforced to limit greenhouse gas emissions, energy-related CO_2 emissions will grow 10.6 % from 2009 to 2027. Combustion of carbon fuels and carbon containing gases lead to the formation of CO_2. The increase of CO_2 concentrations in the atmosphere due to anthropogenic reasons is foreseen as a cause for major climate changes which can possibly be detrimental to the planet [130, 131]. The CO_2 emissions from fuel combustion are projected to touch 35.4 Gt by the year 2035 according to the 2010 World Energy Outlook report [132]. CO_2 can be captured or reduced in three ways i.e. (1) post-combustion, i.e. from flue gases, (2) pre-combustion, i.e. after the gasification process but before combustion of producer gas, and (3) denitrogenation, i.e. using O_2 as a comburent gas instead of air [133].

Current state of the art technologies for the capture of CO_2 from fossil fuel gasification derived producer gas are based on physical solvent washing systems, for example, Rectisol and Selexol processes [134]. Adsorption of CO_2 onto a catalyst/sorbent surface is a promising method of decreasing CO_2 in the gas as it offers potential for energy savings compared to absorption systems and also decreases compression costs [135, 136].

Various sorbents are currently being studied for CO_2 removal [133, 136-145]. Of these, zeolites, hydrotalcites, supported amines, and activated carbons are among the more promising ones. Activated carbon shows lower CO_2 adsorption capacities at low pressure, however at high pressure, activated carbon CO_2 adsorption capacities drastically improve as compared to those of zeolites [145, 146]. Activated carbons also have moderate strength of adsorption for gases which makes it easier to desorb the adsorbates. Moreover, the hydrophobic character and wide variety of precursors available for its synthesis make it a promising sorbent.

The sorbent should have basic functionality for improved CO_2 adsorption. CO_2 being acidic in nature is easily adsorbed onto a basic sorbent surface. To improve the adsorptive capacities of activated carbon, alkalinity can be increased by introducing chemical additives. However, this process can have negative effects upon the carbon properties such as decrease of surface area and loss of porosity. In a study carried out by Kalua and Zdrail [147], MoO_3 was loaded onto an activated carbon, resulting in a decrease in surface area and micropore volume of around 40 % which might have detrimental effects to CO_2 adsorption. Another study [148] evaluating the effect of impregnation of ammoniacal solutions onto the carbon resulted in a partial blocking of the pores. Mesoporous carbons showed a decrease in microporosity indicating that pore blocking is a function of original pore size distribution [148]. Plaza et. al. [133] conducted a study to evaluate the effect of different alkylamine impregnation on activated carbon support for CO_2 capture. They found that the basicity and nitrogen content of the activated carbon increased due to the coating but reduced the capacity of the carbon adsorbent. They attribute this to the reduction in microporous volume of the carbon.

Higher the surface area of the carbon, greater is the CO_2 uptake. In a study carried out by Drage et. al. [136], activated carbon with high surface area (surface area greater than 3000 $m^2 \cdot g^{-1}$) exhibited highest uptake of CO_2 and phenolic resin derived activated carbons had comparable uptake efficiencies on a volumetric basis. The uptake capacities exhibited were higher than those of existing Selexol absorption systems. For the activated carbon, the selectivity of CO_2 adsorption was around 10 times more compared to its capabilities for H_2 adsorption.

The adsorption process in commercial and industrial scale systems is more advantageous if carried out at elevated temperatures (greater than 350 °C) of that of the exhaust flue gas/producer gas. CO_2 uptake was found to decrease from 100 $mg \cdot g^{-1}$ at 30 °C to 40 $mg \cdot g^{-1}$ at 100 °C for a CMFCS sorbent [149]. Ideal conditions for CO_2 removal are low temperature and high CO_2 partial pressure. In a study carried out to evaluate activated carbon as a pre-combustion CO_2 capture sorbent, CO_2 capture capacity and breakthrough time increased with increase in CO_2 partial pressure but decreased with increase in temperature [139]. The authors determined that the maximum CO_2 capture capacity and breakthrough time were obtained for a temperature of 25 °C and a CO_2 partial pressure of 0.3 MPa. Activated carbons showed a lower CO_2 uptake than molecular sieves at low pressures; however at high pressures, the adsorption was higher for the activated carbon than the molecular sieves [150]. Thus, activated carbons require a high CO_2 partial pressure for effective uptake efficiencies.

Activated carbons perform better for CO_2 removal as compared to molecular sieves. Molecular sieve adsorbents resulted in a higher concentration of CO_2 in the product of adsorption of CO_2 from flue gas as compared to that using an activated carbon sorbent in a study conducted by Kikkinides et. al. [151]. A CO_2 recovery of 68.4 % was achieved from flue gas using an activated carbon sorbent with a purity of 99.997 %.

Char has also been evaluated as a CO_2 sorbent. Although the initial results seem promising, the low surface area of char is a barrier for CO_2 capture. Amine enriched fly ash was used as a CO_2 sorbent and gave a 9 % CO_2 capture capacity as compared to commercial sorbents [140]. The fly ash or unburned carbon used in the study was collected from the bag house of a combustion unit and thus, the fly ash is essentially same as char. Although the surfaces of char are rich in oxygen, their low surface area might lead to poor capture of CO_2.

Carbon fiber composite molecular sieve (CFCMS) is a monolithic carbon adsorbent material. It is composed of petroleum pitch derived carbon fiber and a carbon binder derived from phenolic resin. CFCMS is one of the best carbon-based adsorbents of CO_2 due to its high affinity for CO_2 compared to other carbon based sorbents [149, 152]. Sorbent system must be economical to compete with conventional solvent scrubbing systems. A study comparing the cost and economics of sorbent systems to that of monoethanolamine (MEA) absorption systems was carried out by Abanades et. al [137]. The cost of the amount of sorbent required to absorb or react with 1 mole of CO_2 was calculated. The cost per mole of CO_2 was \$0.544 for the MEA system, whereas the same for active carbons was \$0.25. However, the cost of sorbent makeup quantity must be calculated before scale up or comparison of different CO_2 abatement or capture systems since necessary sorption-desorption activity is to be maintained for successful performance of a system.

3.5 Simultaneous removal of contaminants

Simultaneous removal of various contaminants is of prime importance since it offers cost-saving benefits due to lesser unit operations and stages needed. Carbon-based catalysts have several advantages for simultaneous removal of contaminants as they have been proven to be effective for removing of tars, ammonia, H_2S, and CO_2 individually, as discussed previously. Very little research is available attempting simultaneous removal of contaminants as there are numerous challenges involved. Temperature and pressure conditions are crucial variables in this type of attempt to simultaneously remove contaminants as different carbon catalysts show activity at different operating conditions. Simultaneous removal of ammonia and H_2S has been attempted over activated carbon [153] and activated carbon fiber cloth [154]. Concurrent effect of toluene (model tar [17, 110]), ammonia, and H_2S has also been studied over activated carbon [155].

Carbon fiber composite molecular sieve (CFCMS) has been evaluated for removal of CO_2 and H_2S [149].

4 Conclusion and recommendations

Various carbon based materials, especially activated carbon catalysts and sorbents, have been proven to be effective as H_2S sorbents. However, very few studies have been carried out evaluating the effectiveness of these sorbents for the removal of H_2S from biomass-generated producer gas. Based on the published literature covering gas cleaning applications of carbon-based catalysts such as those in coal gasification/combustion, it can be concluded that basic functional groups on the carbon catalyst surface improve H_2S removal efficiencies. Also, Zn, Cu, and Fe impregnated activated carbons are effective catalysts for H_2S removal. Research reveals that to remove the producer gas NH_3, activated carbon catalysts or carbon fibers can be used in a catalytic unit. Modification of the surface groups using metal salts, molybdenum oxide and tungsten oxide improve the NH_3 adsorption efficiency of the carbon catalyst. Strong acidic, sulfonic, and oxygen groups enhance the surface properties of the sorbent for effective NH_3 adsorption.

Amine enriched activated carbon, fly ash, molecular sieves, and carbon fiber composite molecular sieves (CFCMS) all seem to be effective as CO_2 sorbents as long as the process is carried out at low temperature and high pressure conditions. Activated carbons have moderate adsorption strength for CO_2 and must be pre-coated to improve adsorption efficiency. Tar removal can be carried out using carbon-based sorbents having a high surface area. Both, chars and activated carbons are effective catalysts for tar removal. However, high temperatures (greater than 700 °C) are required to obtain high tar removal efficiency as coking reduces at elevated temperatures. Increase in pressure also improves tar decomposition.

For a situation where simultaneous removal of more than one of these contaminants is attempted, the optimum pressure, catalyst pH, and temperature conditions must be carefully selected because the optimum reaction conditions for efficient removal of these contaminants are different. H_2S and CO_2 removal require basic functional groups; whereas NH_3 removal requires acidic functionality. No data was available in literature containing information on functionality of carbon sorbents for tar removal. Using the carbon-based catalysts, CO_2 removal efficiency is high at low temperatures (lower than 100 °C), H_2S and NH_3 is high at moderate temperatures (50 to 300 °C), while tar removal requires high temperature conditions (greater than 600 °C). H_2S and NH_3 removal is effective at low or atmospheric pressure; whereas CO_2 and tar removal require high pressure. All of the above enlisted factors need to be taken into account while attempting simultaneous removal of contaminants from biomass gasification gas.

To develop an effective catalytic gas cleanup system for upgrading producer gas generated through gasification of biomass, further research is needed. Carbon-based catalysts, appearing to be promising prima facie, require further research before scaling up to industrial scale. Special opportunities are in simultaneous removal of several contaminants to reduce the requirements of energy, capital expense, and number of reactors and catalysts.

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CHAPTER III

SYNTHESIS AND EVALUATION OF BIOCHAR-DERIVED CATALYSTS FOR REMOVAL OF TOLUENE (MODEL TAR) FROM BIOMASS GENERATED PRODUCER GAS

Abstract

Challenges in removal of contaminants, especially tars, from biomass-generated producer gas continue to hinder commercialization efforts in biomass gasification. The objectives of this study were to synthesize catalysts made from biochar, a byproduct of biomass gasification and to evaluate their performance for tar removal. The three catalysts selected for this study were original biochar, activated carbon, and acidic surface activated carbon derived from biochar. Experiments were carried out in a fixed bed tubular catalytic reactor at temperatures of 700 and 800 °C using toluene as a model tar compound to measure effectiveness of the catalysts to remove tar. Steam was supplied to promote reforming reactions of tar. Results showed that all three catalysts were effective in toluene removal with removal efficiency of 69 to 92 %. Activated carbon catalysts resulted in higher toluene removal because of their higher surface area (~900 m^2/g compared to less than 10 m^2/g of biochar), larger pore diameter (19 A° compared to 15.5 A° of biochar) and larger pore volume (0.44 cc/g compared to 0.085 cc/g of biochar). An increase in reactor temperature from 700 to 800 °C resulted in 3 to 10 % increase in toluene removal efficiency. Activated carbons had higher toluene removal efficiency compared to biochar catalysts.

Keywords: Biochar, activated carbon, biomass gasification, tar

1 Introduction

Gasification is a thermochemical conversion process in which carbonaceous materials (such as natural gas, naphtha, residual oil, petroleum coke, coal and biomass) react with a gasification medium (such as air, oxygen and/or steam) at high temperatures (600-1000°C) to produce a mixture of gases called producer gas[1-4]. The major components of producer gas are carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), and hydrogen (H_2). Producer gas also contains methane (CH_4), water, some higher hydrocarbons, various inorganic and organic contaminants like char, ash, tar, ammonia (NH_3), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2)[1,5,6]. The impurities in producer gas can cause serious problems with downstream applications of the gas by clogging the process lines, deactivating catalysts, and acting as precursors for toxic emissions[7,8].

Tar can be defined as all organic contaminants having molecular weights higher than benzene[9,10]. Tar contents in producer gas are as high as 0.22 kg/kg biomass[13]. Scrubbers and electrostatic precipitators are effective in reducing the levels of tars. However, these techniques are inefficient because they result in reducing the gas energy content and require disposal of solvents. Catalysts offer a more cost-efficient and an equally effective approach to removal of contaminants[11,12]. Biochar is naturally produced during biomass gasification. Adding value to low-value biochar by using it in applications such as soil amendment, carbon sequestration and gas upgrading has shown researching interest in recent times. Studies have shown that low-cost biochar is a potential catalyst for tar removal[1]. The surface area of biochar is generally low; ranging from 5 m^2/g to around 65 m^2/g depending on the type of biomass and gasification operating conditions[14-

[18]. Effectiveness of the biochar to remove tar can be drastically increased by increasing its surface area and improving its chemical properties. Several studies suggest that increasing surface area of catalyst is critical to efficient tar removal. Seshadri et. al.[19] concluded that a char and dolomite mixture and calcined dolomite were not as active as zeolites and other catalysts evaluated for tar conversion in coal gas streams due to their low surface acidity and low surface area. Donnot et. al.[20] found that the residence time for efficient tar removal is inversely proportional to char surface area. They also investigated the carbon deposition phenomena on the char catalyst and found that at temperatures below 750 °C, a decrease in activity occurs after a short time due to coking. Hence, to understand the effect of coking in our study, experiments were carried out at two different temperatures: 700 and 800 °C.

Activated carbon is a highly porous material with high surface area. Generally, activated carbon can be synthesized by either chemical activation, physical activation, or a combination of chemical and physical activation of a carbon precursor[21]. This activation process gives rise to a highly porous carbon material with high adsorptive properties. The carbon precursor can be any material with carbon as its primary constituent. Various agricultural waste precursors like wheat[22], rice husks[23], sugarcane bagasse[23], corn stover[24], hazelnut[25], and biochar[14] have been used to synthesize this activated carbon. Little data is available in literature on the properties and use of biochar, a by-product from gasification of switchgrass, for the production of activated carbon. Also, activated carbon remains untested as a potential catalyst for tar reduction. Azargohar and Dalai[14] carried out a study to synthesize activated carbon from biochar derived from fast pyrolysis of wood. For this study, we evaluated biochar derived from gasification of switchgrass as a precursor for the synthesis of activated carbon. The effect of ultrasonic impregnation of potassium hydroxide (KOH) onto biochar on the change in the properties of the activated carbon product was also studied. Further, the activated carbon was evaluated for removal of toluene (model tar compound). Previously, a review of carbon-based catalysts for removal of various producer gas contaminants such as ammonia, H_2S, tar, and CO_2 was made[26]. Based on the review, it was concluded that increased surface area of carbon-based catalysts may improve the catalyst performance for removal of contaminants. To validate some of the findings of the review, performance of selected biochar-based catalysts for toluene (model tar compound) removal was evaluated in this study.

No studies have been reported previously for synthesis of activated carbon from biochar derived from gasification of switchgrass. Also, in the present paper, we are investigating the synthesis of activated carbon from biochar using ultrasonication to improve the surface area of the synthesized catalysts. Ultrasonication helps in synthesis of high surface area catalysts [26] and also helps improve particle dispersion[27]. We hypothesize that acidic surface catalyst may help react with a basic contaminant in the producer gas, such as ammonia. However, the acidic surface should not decrease tar removal efficiencies. Acidic surface activated carbon, previously untested for toluene removal, was evaluated in this study. The three synthesized catalysts (biochar, activated carbon, and acidic surface activated carbon) are characterized and evaluated for toluene (model tar compound) removal in fixed-bed reactor experiments. Finally, the effect of reaction temperatures (800 °C and 900 °C) and reaction gas medium (N_2 and producer gas) on toluene removal is also included in this paper.

The specific objectives of this study were to a) synthesize activated carbon from biochar precursors derived from switchgrass gasification and evaluate the effect of ultrasonic potassium hydroxide (KOH) impregnation onto biochar for change in the properties of the activated carbon, b) compare the activated carbon synthesized using biochar from fluidized bed gasification and downdraft gasification, and c) evaluate the effectiveness of biochar and biochar-based activated carbon and acidic surface activated carbon catalysts on the removal of toluene as a model tar compound.

2 Experiment

The experimental design for catalyst synthesis and selection is shown in Fig. 1. Biochar was synthesized in downdraft gasifier and fluidized bed gasifier from gasification of switchgrass. The biochar from both the gasifiers was impregnated with KOH, with and without ultrasonication, and further carbonized to form activated carbons. Biochar and activated carbon derived from downdraft gasifier were selected for further studies because of their higher surface areas than those of biochar and activated carbon derived from fluidized bed gasifier. Further, the activated carbon from downdraft gasifier was coated with dilute ascorbic acid to synthesize acidic surface activated carbon. Finally, the three downdraft gasifier derived catalysts viz. biochar, activated carbon, and acidic surface activated carbon, were evaluated for their toluene removal efficiency in fixed-bed reactor experiments.

2.1 Catalyst preparation

Biochar was generated in a downdraft gasifier[16] and fluidized bed gasifier[17] using switchgrass as a biomass feedstock. The details of the gasifier have been described elsewhere[16,17]. The procedure for the synthesis of the activated carbon was based upon a previous study by Azargohar and Dalai[14]. The biochar was sieved to get the sample with particle size between 150-600 µm. Ten grams of sieved biochar was mixed with ten grams of KOH pellets (Fisher Scientific, Hampton, NH) and 100 mL distilled water to obtain 1:1 mass ratio of KOH to biochar. A 1:1 mass ratio of KOH to biochar is used based upon promising results obtained previously[14]. This mixture was stored overnight to allow sufficient time for KOH to access biochar pores. To synthesize activated carbon using an ultrasonication method, the mixture was sonicated (Fisher Scientific 550 Sonic Disembrator, Pittsburgh, PA) for 0.25 and 0.5 h at 30% power. The mixture was then dried at 110 °C overnight in an oven (Vulcan 3-550, Neycraft). The biochar was carbonized[14,28,29] in a tubular catalytic reactor made of quartz glass with 22 mm inner diameter and 914 mm length (schematic shown in Fig. 2) with nitrogen flow. The temperature of the reactor bed was raised from 25 to 200 °C at 3 °C/min and held for 1 h. This was followed by ramping up the temperature at 10 °C/min to 700 °C and held at that temperature for 2 h. The reactor temperature was controlled by a heating jacket (Carbolite furnace model TVS 12/600, WI, USA). The bed temperatures were monitored using thermocouples and a constant temperature zone was identified before carrying out any experiments. The inlet lines of the reactor were heated and kept at 200 °C using heat tapes (model STH 051-020, Omega Engineering INC, Stamford, CT) to preheat the nitrogen gas supply. After carbonization, the bed temperature was decreased from 700 °C to 25 °C overnight under nitrogen flow in the reactor. The cooling procedure was done to prevent combustion of biochar upon immediate exposure to air. The heat treatment was followed by washing with distilled water and further with 0.1 M HCl, to help develop the pore structure. The samples were dried overnight at 120 °C. Activated carbon derived from downdraft gasifier biochar was selected for synthesis of acidic surface activated carbon due to its higher surface area. Acidic surface activated carbon was synthesized by stirring the activated carbon with 10 % dilute citric acid (1:1 volumetric ratio). The coated activated carbon was further dried at 110 °C for 4 h in a furnace oven to give acidic surface activated carbon.

2.2 Catalyst characterization

Characterization was carried out on downdraft gasifier biochar and downdraft gasifier activated carbon. The downdraft gasifier catalysts were selected for characterization and testing because they had a higher surface area than those of fluidized bed gasifier catalysts. The catalysts were characterized before and after use in the catalytic reactor experiments. Proximate analysis of biochar and activated carbon was performed according to the ASTM standard D3172-07a[30]. Analysis of Brunauer-Emmett-Teller (BET) surface area and pore diameter and volume was done using a surface area analyzer (Quantachrome model 1-C, Boynton Beach, FL). Nitrogen isotherms were measured at 77 K for relative pressure (P/P_0) values ranging from 0.1 to 0.3. The catalysts samples were outgassed for 24 h at 300 °C under helium flow before calculating their surface areas. Temperature programmed oxidation (TPO) was carried out using 5 % O_2 in helium gas; whereas chemisorption experiments were carried out using CO_2 gas using the same Quantachrome equipment. X-ray diffraction (XRD) imaging was performed using Bruker D-8 Advanced X-ray powder diffractometer (Bruker AXS, Madison, WI). Fourier transform infrared analysis (FTIR) was done using a Nicolet 6700 spectrometer (ThermoFisher Scientific, Waltham, MA). The samples were powdered and the powder sampling accessory was used for the FT-IR analysis. TGA characterization was performed in a thermogravimetric analyzer (model: Versa Therm, ThermoFisher Scientific, Waltham, MA). Scanning electron microscopy (SEM) images were captured using a JEOL JSM-6360 and FEI Quanta 600F Scanning Electron Micrographs at magnifications of 100-1000x. The catalysts were placed in the multi-specimen holder of the scanning electron microscope without gold sputtering. Different magnifications were used at accelerating voltages of 15 kV and 20 kV. Energy-dispersive X-ray spectroscopy (EDS) spectra were taken using EVEX EDS (Princeton, NJ) at different magnifications with accelerating voltages of 20 kV.

2.3 Toluene removal with catalysts

Toluene was selected as a model tar compound because toluene is the largest component of the tar (13 % w/w of tar) other than benzene and has been used previously as a model tar compound [28,29,31]. Biochar and synthesized activated carbon catalysts derived from downdraft gasifier were evaluated for their effectiveness to decompose toluene in a high-temperature tubular reactor. Based on the surface area results obtained (section *3.1*), three catalysts were selected as catalysts for toluene removal (Fig. 1). The catalysts selected were downdraft gasifier biochar, activated carbon derived from downdraft gasifier biochar, and acidic surface activated carbon, because their surface areas were greater than fluidized bed gasifier biochar and fluidized bed gasifier biochar-derived activated carbon respectively. The reactor (Fig. 2) consisted of a stainless steel reactor tube (0.0127 m inner diameter, 0.91 m length). This tube was placed in the tube furnace used for carbonization. Experiments were carried out in two sets. The first set of experiments consisted of toluene in nitrogen flow to observe gas formation and reactions. The second set of experiments was carried out with gas mixture with a composition similar to producer gas (5.15 % H_2, 7.49 % CH_4, 16.79 % CO_2, 19.30 % CO, and balance N_2) so as to observe the effect of producer gas components on the toluene removal process. The temperature of the bed was monitored using a K-type thermocouple placed in the middle of the catalytic bed. Liquid syringe pumps (KD Scientific, Holliston, MA) were used to inject toluene into the reactor.The toluene was vaporized before mixing with the gas stream. Gas samples were collected in syringes and analyzed using gas chromatograph (Agilent 5890 Series II, Santa Clara, CA) calibrated for all the producer gas components using various calibration mixture cylinders purchased from Stillwater Steel Inc. (Stillwater, OK). One gas sample was taken every 20 minutes. Toluene removal efficiency was defined as

$$X=\frac{(C_{in}-C_{out})}{C_{in}}\times 100$$

where, X is the percent removal of toluene, and C_{in} and C_{out} are the concentrations of toluene (% volume) at the inlet and outlet, respectively. The gas residence time, τ ($kg \cdot m^3 \cdot h^{-1}$), was defined as

$$\tau=\frac{w}{v_0}$$

where, w is the weight of the catalyst (kg) and v_0 is the flow rate of the gas mixture at the catalyst bed (m^3/h). The gas residence time was approximately 0.035 $kg \cdot h \cdot m^{-3}$ for biochar and 0.123 $kg \cdot h \cdot m^{-3}$ for activated carbons. Quantities of catalysts used for the experiments were 1 g of biochar obtained from downdraft gasification of switchgrass and 0.35 g of activated carbon and acidic surface activated carbon, synthesized using ultrasonication from the same downdraft gasifier char as used in these experiments. A lower quantity of activated carbon was used since activated carbon has lower density than biochar. Different catalyst quantities were used to ensure same bed height (0.014 m) and bed volume (4.39×10^{-8} m^3) for all the experiments.

2.4 Statistical analysis

Statistical Analysis of the data was carried out with the help of SAS 9.3 (Carey, NC) statistical software. Surface area data was analyzed using two-sample t-test assuming $\alpha = 1$ %. Quality of data obtained from toluene removal with catalysts experiments was confirmed by checking normality of data from comparison of data histogram with a normal probability curve. A bell-shaped curve was obtained for the data. General linear model (GLM) procedure was used to analyze the data further. Post-hoc multiple comparisons were performed using LSD and Duncan's tests. Finally, correlations among the variables were also evaluated.

3 Results and discussion

3.1 Synthesis and surface characterization of fresh catalysts

The area-volume-pore size summaries of activated carbon and biochar derived from the two types of gasifiers is shown in Table 1. The biochar obtained from the downdraft gasifier had a higher surface area (900 m^2/g) than that obtained from the fluidized bed gasifier (200 m^2/g). This is primarily due to the different configurations of the two gasifiers which result in differences in gasification conditions[16-18].

A significant increase in surface area ($p < 0.01$) was observed upon ultrasonication of the biochar obtained from downdraft gasifier (Table 1). Also, the increase in surface area with increase in ultrasonication time was found to be significant ($p < 0.01$). On the other hand, very little increase in surface area was observed (Table 1) for the activated carbon synthesized using ultrasonication from fluidized bed gasifier compared to that without using ultrasonication ($p > 0.01$). Ye at al. (2004) reported that ultrasonication resulted in homogeneous dispersion of catalyst particles[32] which may have played a role in improving contact of catalyst with the gas stream. Increase in contact of contaminants with the catalyst surface may lead to increase in tar removal efficiencies. TGA study carried out to analyze the thermal stability of biochar during activation process (Fig. S4, supporting information) shows that there is a 19.2 % decrease in residual weight percent. This weight loss is consistent with the results obtained by Azargohar and Dalai[14]. During the activation process, volatiles evolve from interior of the biochar, thus causing decrease in weight. This loss in weight decreases the yield of activated carbon obtained. However, volatiles shown by the weight loss does not consist of ash. Ash consists of inorganic elements in biochar (Table S2, supporting information) and is stable at elevated temperatures and does not decompose below 1000 °C. After carbonization of biochar to obtain activated carbon, the activated carbon is washed to help develop porosities. During the washing step, minerals are washed away causing a decrease in ash content (as high as 77 %) in the activated carbon sample (Table S1, supporting information). The ash content of biochar obtained from fluidized bed gasification of switchgrass was 78.3 % whereas the same for downdraft gasifier biochar was 21.3 %. Assuming a 20 % decrease in weight during carbonization step and 100 % removal of ash from the sample during washing step, approximately 16 to 72 % activated carbon yield can be obtained from biochar derived from fluidized bed and downdraft gasifiers. The high yield of activated carbon obtained is essential for commercialization of activated carbon from biochar obtained from biomass gasification processes.

3.2 Surface characterization of used catalysts

The surface characteristics of used catalysts (Table 2) show a significant decrease ($p < 0.01$) in surface area. A decrease of 25.6 % was observed in surface area of the used activated carbons (about 700 m^2/g) as compared to that of the fresh activated carbon (about 900 m^2/g). The pore radius decreased from 15 to 18 A° to around 11 A° for all the catalysts. There was an 88 % decrease in the pore volume of biochar, possibly due to coking of the catalyst. Coke formation usually occurs due to deposition of graphitic carbon on the surface of biochar-based catalysts and is well documented in literature[33-36]. These decreases in pore radius and pore volume may prove to be a barrier for commercialization of biochar as catalysts. Regeneration of the catalysts might be needed to improve its performance over longer time on stream[37]. The decrease in surface area of activated carbons (25.6 %) was comparatively lesser than that of biochar (75 %) when used as catalyst for toluene removal.

3.3 Proximate and elemental analysis of catalysts

Ash (Table S1, supporting information) and mineral (Table S2, supporting information) contents of biochar were higher than those of activated carbons. The proximate analysis (Table S1, supporting information) indicated that ash content of biochar derived from the fluidized bed gasifier (78.3 %) was much higher than that of biochar derived from the downdraft gasifier (21.2 %). However, the activated carbons derived from both biochars contained low ash (about 1 %) due to several wash cycles used for the synthesis of the activated carbon. All catalysts, except the biochar derived from the fluidized bed gasifier, contained high fixed carbon (75 to 90 %). Elemental analysis (Table S2, supporting information) shows that biochar obtained from the fluidized bed gasifier contained low amounts of total carbon (1.4 %) and total nitrogen (0.05 %); whereas biochar from the downdraft gasifier contained high amount of total carbon (64.8 %). Both the activated carbons contained high amounts of total carbon (64 to 73 %) and nitrogen (0.7 to 0.8 %) because the ash content was lowered due to several wash cycles during their synthesis. These results imply that not all biochar generated from biomass gasification may be suitable for use in specific applications such as producer gas contaminant removal or as gasification in-bed catalysts. Biochar consists of ash (minerals) and char (carbon) as its primary constituents; generally, high carbon content seems promising for tar removal as ash has been found to be ineffective for tar removal[38]. Hence, only biochar and activated carbon from downdraft gasifier (with much lower ash content) were selected for further study on toluene removal.

3.4 Crystallinity, elemental, and microscope analysis of catalysts

As shown in Scanning Electron Microscopy (SEM) images of fresh catalysts (Fig. 3), biochar consisted of background materials, which were possibly the solid residues present in the biochar sample. Solid residues may contain unburnt biomass particles during the gasification process. Also, the ends of the biochar particles were observed to be closed and not porous. On the other hand, the activated carbon showed clear pore developments that may have resulted in larger surface area. When the volatiles from the char leave the char particle, they generate pores in the carbon particle. These can clearly be observed in the images of activated carbon. The thermal treatment and several wash cycles of biochar cause the solid residues to volatilize or wash out and hence, no background matter was observed in the images of activated carbon.

Scanning electron microscopy (SEM) images of the used catalysts (Fig. 4) show high amount of coking in the biochar as evident from the round structures blocking the pores of the carbon filament. Images of the used activated carbons show changes in catalyst structure. This could also be the result of coking of the catalysts. Decreases in surface area, pore volume and pore diameter of the activated carbon were observed (Table 2) due to blocking of the pores also seen from the SEM images.

Fourier transform infrared (FTIR) spectroscopy images (Fig. S1, supporting information) show development of aromatization in the activated carbon (top curve) since C-H bonding was absent. Biochar samples showed out-of-plane bending of ring C-H bonds (peaks between 675/cm and 900/cm) and skeletal vibrations due to ring carbon-carbon stretching (peaks between 1400/cm and 1600/cm). These interactions were absent in activated carbon (top). Tar samples for FTIR analysis were obtained by scraping representative samples from inside of the cyclone of fluidized bed gasifier after a gasification run. Cyclone is a unit of the gasification system where particulates are collected as the producer gas passes through. Tar deposition usually occurs on the colder sections of the cyclone units. Results (Fig. S2, supporting information) indicate the presence of phenolic compounds, primary alcohols and aliphatic ethers. These results are in agreement with those of Wei et. al.[39]. Furanic compounds (chlorobenzofurandione) were also identified in the tar. Furans are commonly found in pyrolysis oils[40].

X-ray diffraction (XRD) images (Fig. S3, supporting information) show that silica was the only easily identifiable element in fresh biochar ($2\Theta = 28.8°$); whereas several elements were identifiable in used biochar due to its higher mineral content. In fresh activated carbon, not many elements can be easily identified due to its low ash content after several wash cycles. However, silica oxide was identified in the used activated carbon due to its lower carbon content ($2\Theta = 21.6°$).

Energy-dispersive X-ray spectroscopy (EDS) spectra were obtained for fresh and used catalysts. The elements observed in the samples (Table S3, supporting information) showed that silica content was the highest in fresh biochar catalyst (82.5 %). Minerals such as magnesium, potassium were not as easily identified in the used biochar sample as compared to those in the used activated carbon. This may be a result of the high silica content in the fresh biochar to begin with. Silica, calcium, potassium, and iron were the major elements found in activated carbon samples.

3.5 Catalyst weight loss characteristics

As seen in the weight loss curve of tar (Fig. S4, supporting information), most of the lighter volatile fractions in the tar decomposed first followed by the heavier fractions. The heavy and high boiling point (greater than 300 °C) fractions decomposed gradually. Activated carbon began to decompose at a temperature of 400 °C (Fig. S4, supporting information) while biochar decomposition began at around 300 °C (Fig. S4, supporting information). Coking is a major drawback of carbon based catalysts. Coke is described as several kinds of carbon deposits formed on catalysts. This coke can be pyrolytic, encapsulating, or whisker coke[41]. The coking tendency of carbon containing catalysts can be controlled by impregnating the catalysts with other elements such as rubidium, nickel supported on MgO[42].

3.6 Temperature programmed oxidation (TPO)

TPO profiles at 15 °C/min (Fig. S5, supporting information) show that activated carbon had a higher area under the signal vs. temperature curve (10103 mV·°C) compared to biochar (2279 mV·°C). This difference in area possibly indicates that activated carbon had a higher catalytic activity compared to biochar. Also, this activity began at the same temperature for both the catalysts (about 300 °C) but lasted longer (about 800 °C) for activated carbon compared to biochar (about 650 °C). Also, the areas under the signal vs. temperature curves increased upon increasing the heating rate from 15 °C/min to 35 °C/min for biochar. This increase in area under the curve with increase in heating rate possibly indicates that biochar has lower coking tendency at higher heating rates.

3.7 CO_2 chemisorption

CO_2 chemisorption results showed strength of adsorption onto the catalysts. A known quantity of CO_2 was injected onto the catalyst surface and a vacuum was pulled to identify strong and weak adsorptive sites and whether adsorption was controlled by physiosorption or chemisorption. It can be seen in Fig. S6 (see supporting information) that weak adsorption is higher (0.5 mmol/g to 1.8 mmol/g) compared to strong adsorption (0.1 mmol/g) in the pressure ranges that were evaluated. Higher weak adsorption than strong adsorption implies that chemisorption is weak onto the activated carbon surface. This implies that gases are weakly adsorbed onto the carbon surface and could easily be desorbed using regeneration techniques. Also, the adsorptive capacity is as high as1.8 mmol/g at 60 kPa indicating high sorption capacity.

3.8 Toluene decomposition study

Toluene in nitrogen

Toluene removal efficiencies of both activated carbon catalysts were significantly higher than that of biochar at 800 °C (Table 3). The toluene removal efficiencies for both activated carbons were not significantly different at 700 °C. Also, at 700 °C, activated carbon showed the highest toluene removal efficiency (86.3 %), whereas at 800 °C, acidic surface activated carbon showed the highest removal efficiency (92.1 %) among all the catalysts. Biochar showed the highest average standard deviation of toluene removal efficiency among all the catalysts indicating that biochar performance was variable during the 4 h experiment, possibly due to coking of the catalyst. It was observed that toluene removal efficiencies decreased with time on stream (Fig. S7 and Fig. S8, supporting information) for all the catalysts at 800 °C. This was confirmed by observing the analyses of covariances plot that had a decreasing linear trend as well as from the Pearson's correlation coefficient 'r' that was -0.27 at 800 °C. The Pearson's value (r = -0.27) at 800 °C indicates that there is weak negative correlation between time on stream and toluene removal efficiency. This further implies that the catalysts deactivate slowly during the time period the catalysts were tested. Toluene removal efficiencies were as high as 92.1 and 86.3 % for activated carbons and biochar, respectively. These values are comparable with those of commercial catalysts such as fluid catalytic cracking catalysts and transition metal (Ni) based catalysts reported in previous studies[38]. The commercial catalysts are more expensive and are easily deactivated[43] by coking and poisoning by other gasification contaminants such as H_2S.

Gases evolved during the tests (Table S4, supporting information) show that concentration of CO, CO_2, and H_2 were the highest at 800 °C for activated carbon among the three catalysts. The methane concentration remained relatively constant for all catalysts and temperatures. Formation of methane indicates that methane reforming reactions may be occuring[35]. The reaction mechanism for methanation is as follows:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O$$

The gas concentration for biochar did not change with temperatures; whereas an increase in gas evolution with temperature was observed for the two activated carbons.

Toluene in producer gas

No significant difference was observed in the toluene removal efficiencies for the two activated carbons at both 700 and 800 °C in producer gas medium (Table 3). However, the toluene removal efficiency of biochar was significantly different than those of activated carbon catalysts. Activated carbons exhibited better performance (79 to 88 %) in toluene removal efficiency from producer gas (Table 3) compared to biochar. For all the catalysts, the toluene removal efficiencies in the presence of producer gas were lesser than those obtained in the presence of nitrogen gas. This indicates that producer gas components decrease toluene removal efficiency possibly due to their adsorption on the catalysts[36]. Also, the toluene removal efficiency of acidic surface activated carbon (about 79 %) was less than that of activated carbon (about 82 %) at 700 °C; although the mean toluene removal efficiencies of the two catalysts were not significantly different. The removal of other producer gas contaminants, such as NH_3 which are basic in nature can be improved using an acidic surface[44]. Thus, although the lower toluene removal efficiencies suggest that acidic surface activated carbon is not effective in improving toluene removal efficiencies, the removal could be sufficiently high for use of acidic surface activated carbon for simultaneous removal of producer gas contaminants. Acidic groups on catalyst surface impart a hydrophilic and polar characteristic to the catalyst[45]. Polar sites on the catalyst surface may be reacting unfavorably with toluene, thus causing a decrease in toluene removal efficiency. The Pearson's correlation coefficient was found to be -0.48 at 700 °C and -0.45 at 800 °C for toluene removal efficiency and time on stream. Negative Pearson's correlation value indicates that there is a gradual decrease in toluene removal efficiency for the catalysts (Fig. S9 and Fig. S10, supporting information). This was also confirmed from the analysis of covariance plots for the catalysts. The larger negative Pearson's 'r' value in producer gas medium (r = -0.45 and -0.48) compared to that in nitrogen gas medium (r = 0.037 and -0.27) at 700 and 800 °C, may be an indication that producer gas components promote carbon formation reactions and coking of the catalyst. The gas concentration profiles (Table S5, supporting information) show an increase in CO, CO_2, and CH_4 gas formation at a temperature of 800 °C for both the activated carbons. A high level of H_2 (8.6 %) was found for the activated carbons at 800 °C indicating an improvement in gas calorific value. The energy in calorific value would help overall energy efficiency. CH_4 concentrations decreased for all the catalysts in the presence of steam possibly indicative of reverse methanation reaction[33]. Various reactions mechanisms have been hypothesized to occur during tar cracking[33,35,46]. A summary of various types of possible reactions follows:

$C_7H_8 + 7H_2O \leftrightarrow 7CO + 11H_2$.....Steam reforming reaction

$C_7H_8 + 7CO_2 \leftrightarrow 14CO + 4H_2$.....Dry reforming reaction

$C_7H_8 \leftrightarrow 7C + 4H_2$.....Carbon formation

$C_7H_8 + 10H_2 \leftrightarrow 7CH_4$.....Hydrocracking

$CO + H_2O \leftrightarrow CO_2 + H_2$.....Water gas shift reaction

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$.....Methanation reaction

$C + 2H_2 \leftrightarrow CH_4$.....Hydrogasification reaction

$C + H_2O \leftrightarrow CO + H_2$....Water gas reaction

$C + CO_2 \leftrightarrow 2CO$.....Boudouard reaction

Toluene removal efficiencies at 800 °C were significantly different than those at 700 °C (Table 3) for both the gas mediums. An increase in temperature improved the toluene removal efficiencies for all the catalysts tested and this trend is consistent with available literature on catalytic tar removal[33,35,47].

4 Conclusion

Three catalysts, biochar, activated carbon and acidic surface activated carbon, were synthesized and evaluated for toluene removal. Compared to biochar, activated carbon synthesized from biochar had higher surface area (about 900 m^2/g) and pore volume (about 0.4 cc/g). All three catalysts i.e biochar, activated carbon, and acidic surface activated carbon, were effective in tar removal (with removal efficiency of 69 to 92 %). Activated carbon catalysts resulted in higher (92 %) toluene removal efficiency than biochar (79 %). At 700 °C reactor temperature, activated carbon had the highest toluene removal efficiency of 86 % among the catalysts tested, whereas, at 800 °C, acidic surface activated carbon had the highest removal efficiency of 92 %. However, in the presence of producer gas, activated carbon performed better than acidic surface activated carbon at both the temperatures. Decreases in surface area during 4 h run were 88 and 25 % in biochar and activated carbons, respectively. The mean toluene removal efficiency for biochar was significantly lower from that of activated carbon catalysts. Although toluene removal efficiency of activated carbon with acidic surface was lesser than other catalysts, the increased acidity of the activated carbon surface may aid in removal of ammonia from the producer gas. Further evaluations of the biochar-based catalysts are needed for lifetime performance, simultaneous removal of ammonia, H_2S, and tar, and biomass-generated producer gas with tar, to determine their commercial potential.

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Supporting Information

Fig. S1 and Fig. S2 contain FT-IR spectra for char, activated carbon, and tar. Fig. S3 contains XRD images for fresh and used catalysts. Fig. S4, Fig. S5, and Fig. S6 are TGA, TPO, and CO_2 chemisorption analysis results respectively for the catalysts. Fig. S7, S8, S9, and S10 are graphs of toluene removal efficiency vs. time on stream for the tested catalysts at different temperature and gas mediums. Table S1, Table S2 and Table S3 contain proximate analysis, elemental analysis, and EDS spectra results for fresh and used catalysts respectively. Table S4 and Table S5 contain average gas concentrations obtained for nitrogen medium and producer gas medium respectively.

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FIGURES:

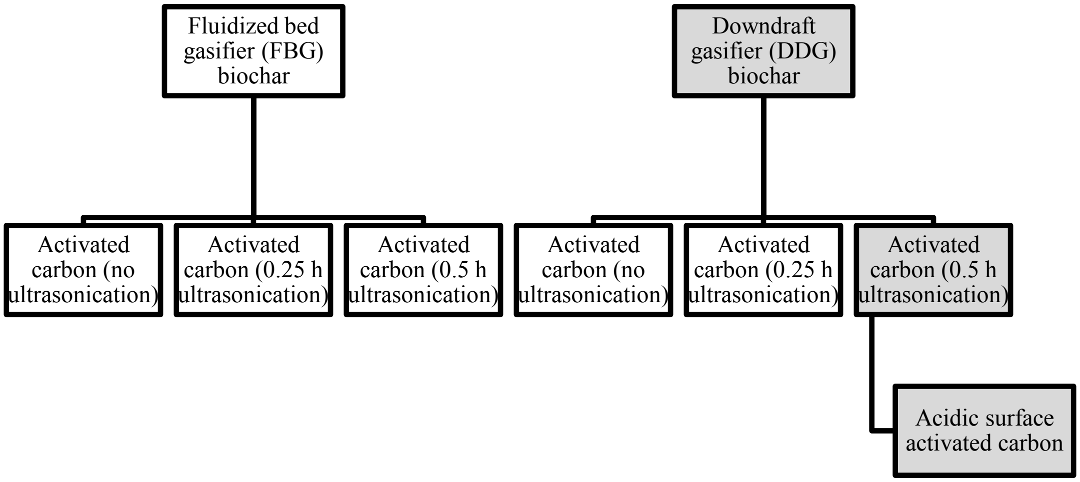


Fig. 1: Design of experiments. Grey blocks indicate catalysts selected for toluene removal study.

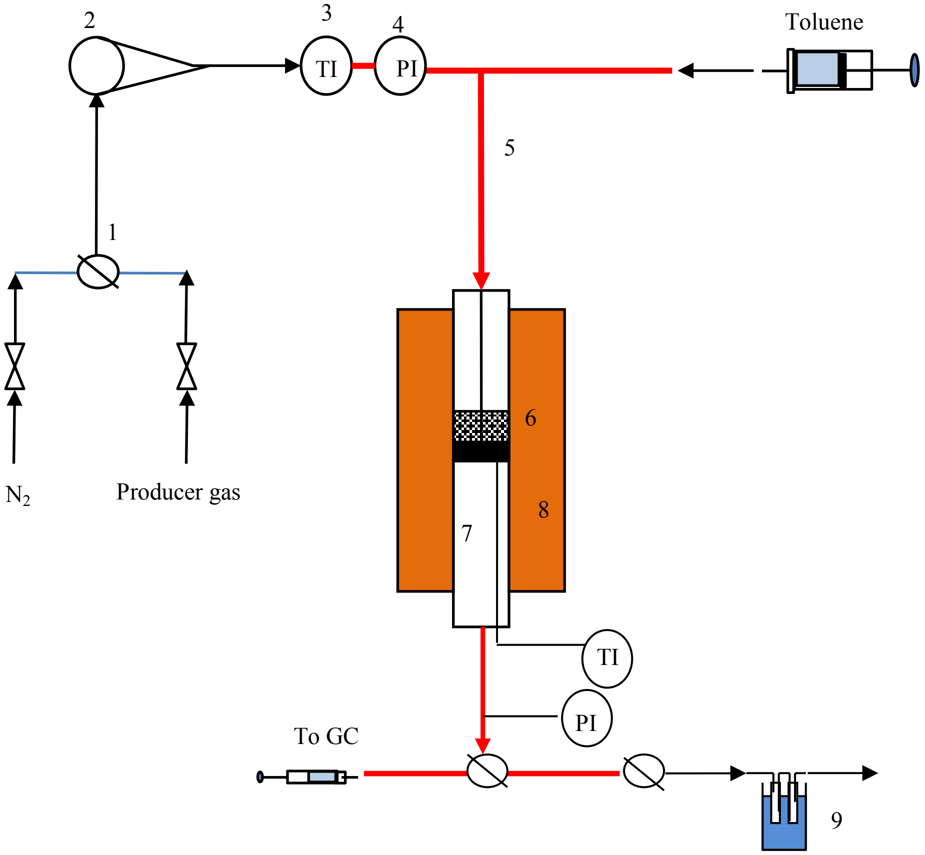


Fig. 2. Process schematic of reactor (1. Ball valve; 2. Rotameter; 3. Temperature indicator; 4. Pressure indicator; 5. Heated line; 6. Catalyst bed; 7. Tubular reactor; 8. Tubular furnace; 9. Water condenser)

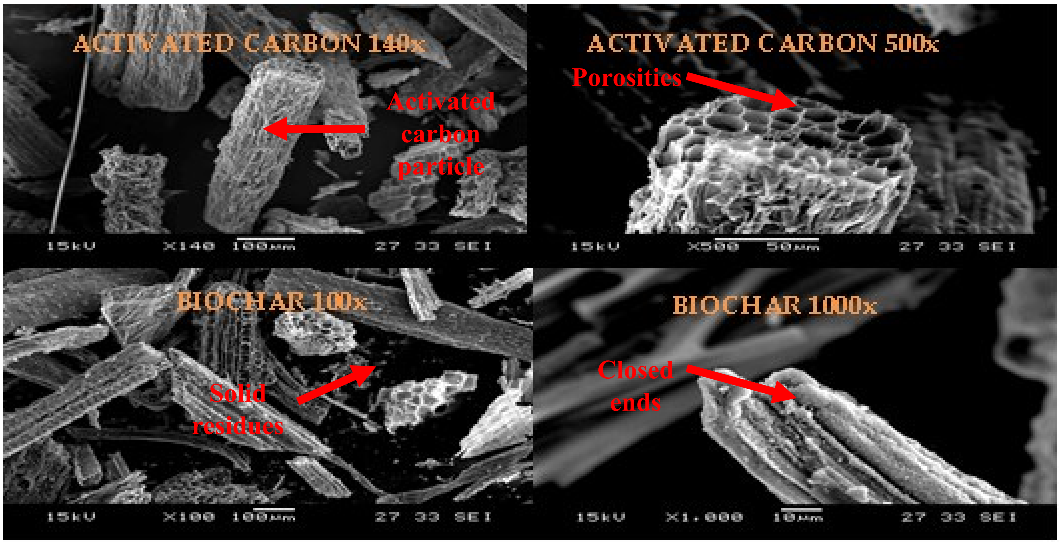


Fig. 3. Scanning electron microscopy images of fresh activated carbon (top two images) and biochar (bottom two images) synthesized from downdraft gasifier.

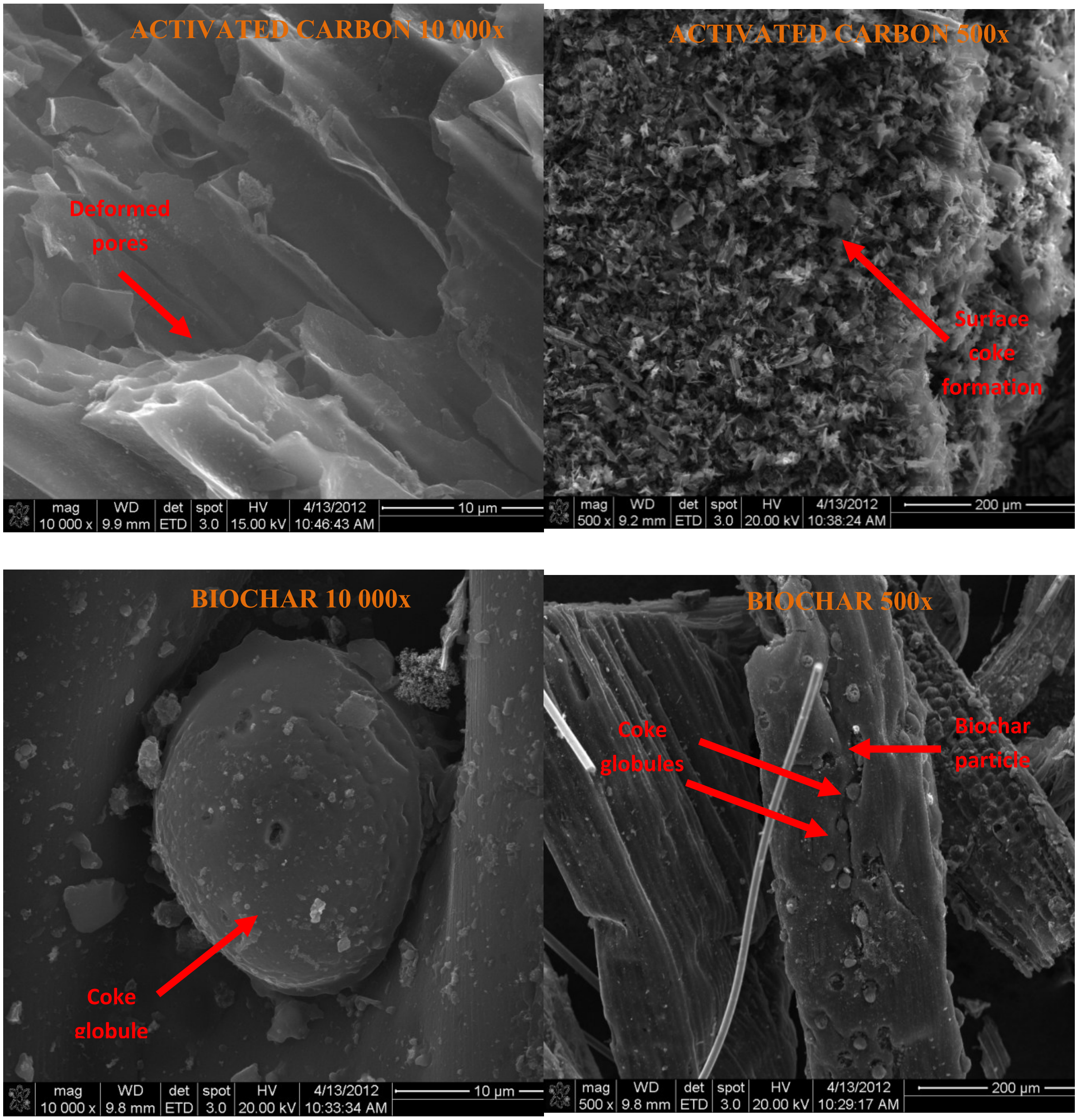


Fig. 4. Scanning electron microscopy images of used catalysts: activated carbon (top two images) and biochar (bottom two images) synthesized from downdraft gasifier. (Toluene removal tests were conducted at 700 °C in producer gas atmosphere).

Table 1: Effect of ultrasonication on surface and pore characteristics of activated carbons obtained from downdraft and fluidized-bed biochars.

	Downdraft Gasifier				Fluidized Bed Gasifier			
	Biochar	Activated Carbon	Activated Carbon (15 min. ultrasonication)	Activated carbon (30 min. ultrasonication)	Biochar	Activated Carbon	Activated Carbon (15 min. ultrasonication)	Activated carbon (30 min. ultrasonication)
BET Surface Area (m^2/g)	64	889	911	944	2	200	210	207
Average Pore Radius (A°)	15.5	18.9	18.9	19.1	15.0	18.9	19.0	19.0
Total Pore Volume (cc/g)	0.09	0.42	0.44	0.45	0.02	0.43	0.42	0.43

Table 2: Surface and pore characteristics of downdraft-gasifier derived catalysts after use in fixed-bed reactor experiments.

Characteristic	Used Biochar	Used Activated Carbon	Used Acidic Surface Activated Carbon
BET Surface Area (m^2/g)	16.7	702.4	632.8
Pore Radius (A°)	11.2	11.2	11.1
Pore Volume (cc/g)	0.01	0.39	0.35

Table 3: Mean toluene removal for activated carbon catalysts and biochar at toluene flow rate of 2 ml/h and N_2/producer gas flow rate of 1 scfh, (standard deviation for 2 experiments).

Catalyst	Mean Toluene Removal* (%)			
	Toluene with N_2		Toluene with producer gas	
	700°C	800°C	700 °C	800°C
Biochar	$78.65^{a\ *\$} \pm 12.05$	$81.01^{b*} \pm 11.83$	$69.18^{b\$} \pm 11.89$	$78.83^{b*} \pm 4.74$
Activated carbon	$86.28^{a\$} \pm 7.7$	$91.69^{a*} \pm 4.9$	$82.08^{a\&} \pm 7.73$	$88.55^{a\$} \pm 6.62$
Acidic surface activated carbon	$80.78^{a\$} \pm 7.7$	$92.09^{a*} \pm 8.4$	$79.13^{a\$} \pm 7.78$	$88.14^{a*} \pm 7.89$

*Means followed by same letter within a column or followed by same symbol within a row are not significantly different ($\alpha = 0.05$)

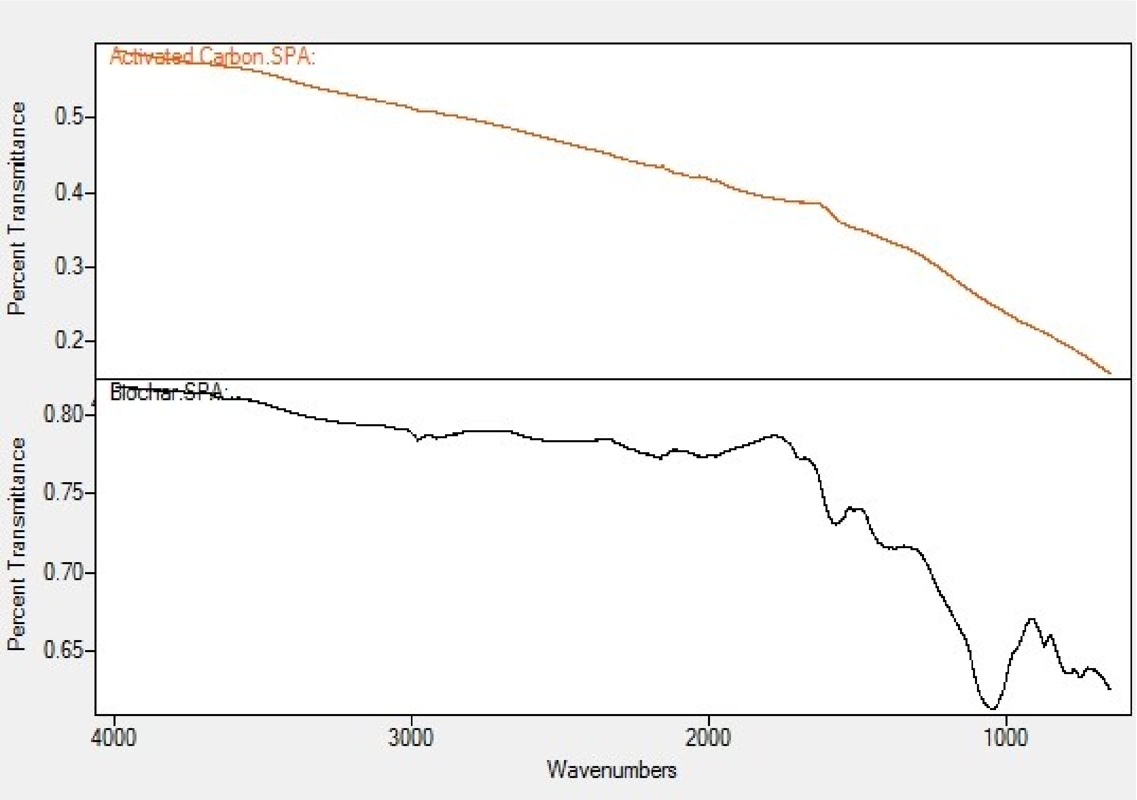


Fig. S1. FT-IR spectroscopy images of fresh activated carbon (above) and fresh biochar (below). Catalysts were derived from downdraft gasifier.

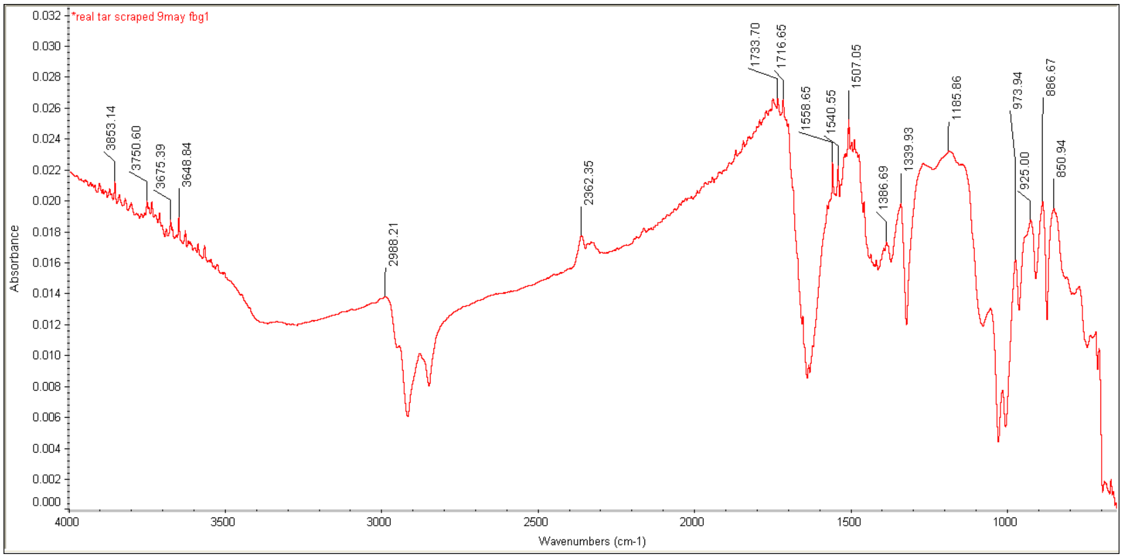
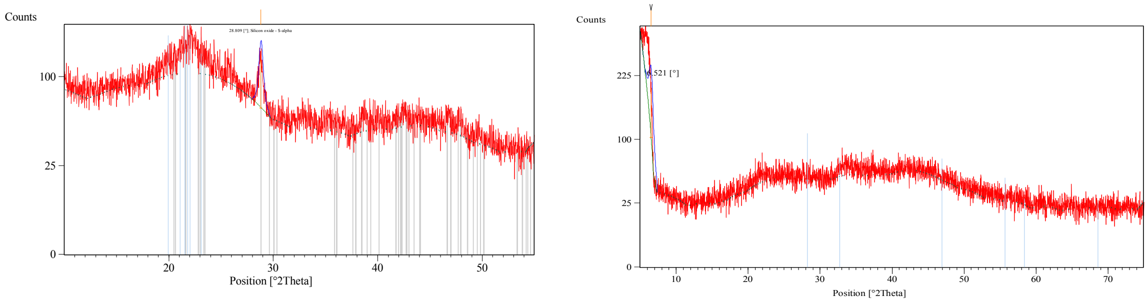
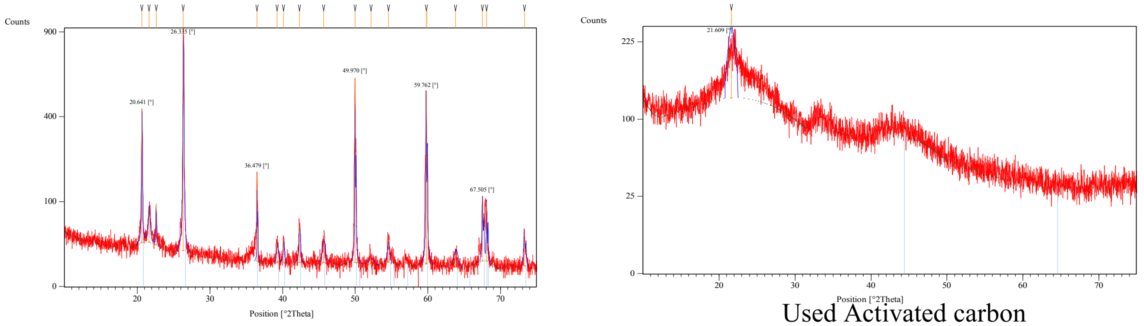


Fig. S2. FT-IR spectra of tar collected from cyclone of fluidized bed gasifier.



Fresh Biochar

Fresh Activated carbon



Used Biochar

Used Activated carbon

Fig. S3. XRD analysis counts vs. position (°2 theta) of fresh and used catalysts.

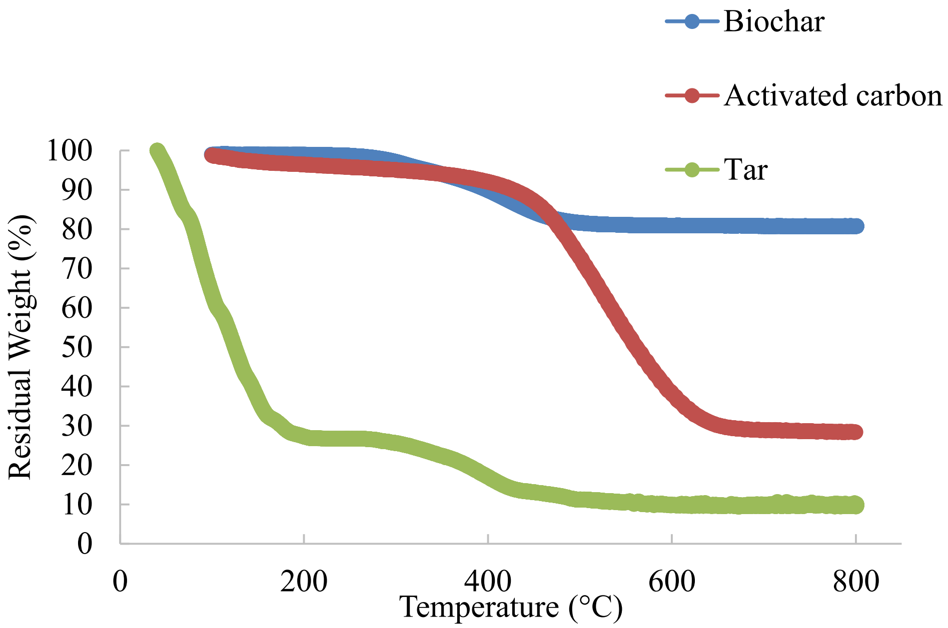


Fig. S4. Weight loss profiles of biochar and activated carbon derived from downdraft gasifier, and tar obtained from cyclone of fluidized-bed gasifier.

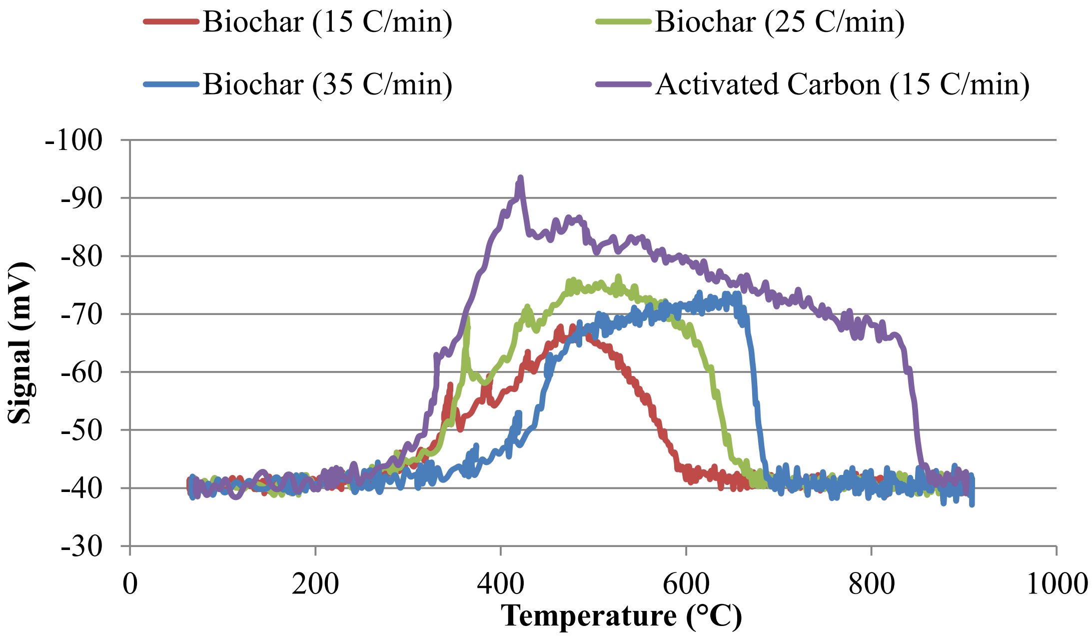


Fig. S5. Temperature programmed oxidation (TPO) profiles for biochar at heating rates of 15, 25, and 35 °C/min; and activated carbon at a heating rate of 15 °C/min.

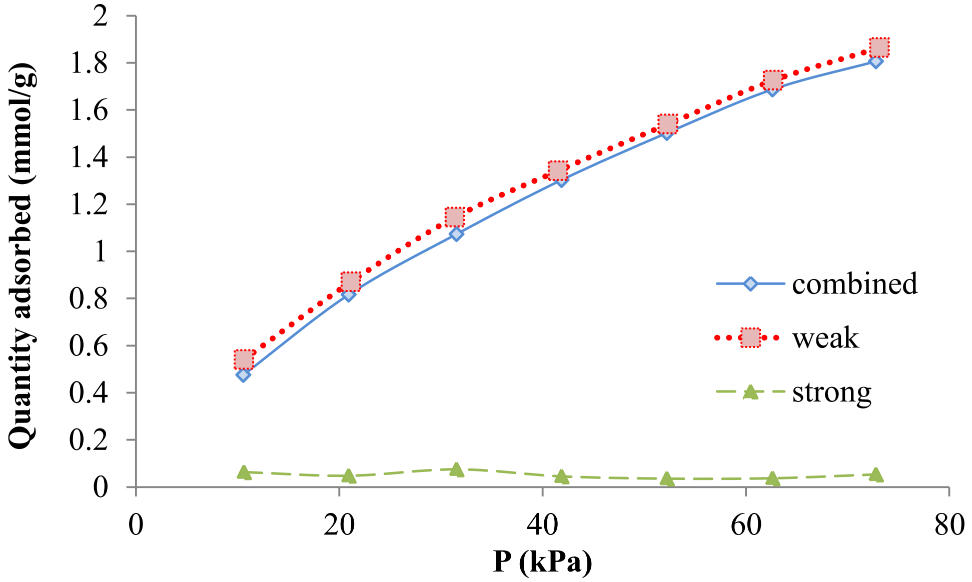


Fig. S6. CO_2 chemisorption on activated carbon at 40 °C.

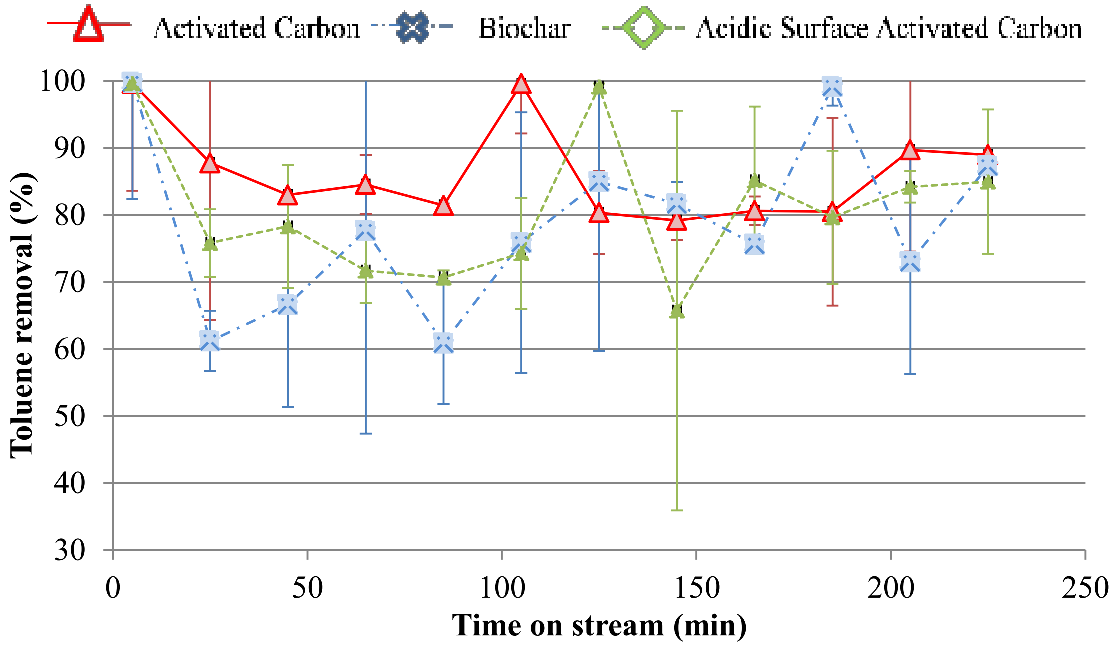


Fig. S7. Percent toluene removal vs. time on stream for biochar and activated carbons at 700 °C and nitrogen atmosphere. Experimental conditions were weight of activated carbon = 0.35 g, weight of char = 1 g, nitrogen flow = 1 scfh, steam flow = 24 ml/hr. Error bars represent standard deviation (two replications for each data point).

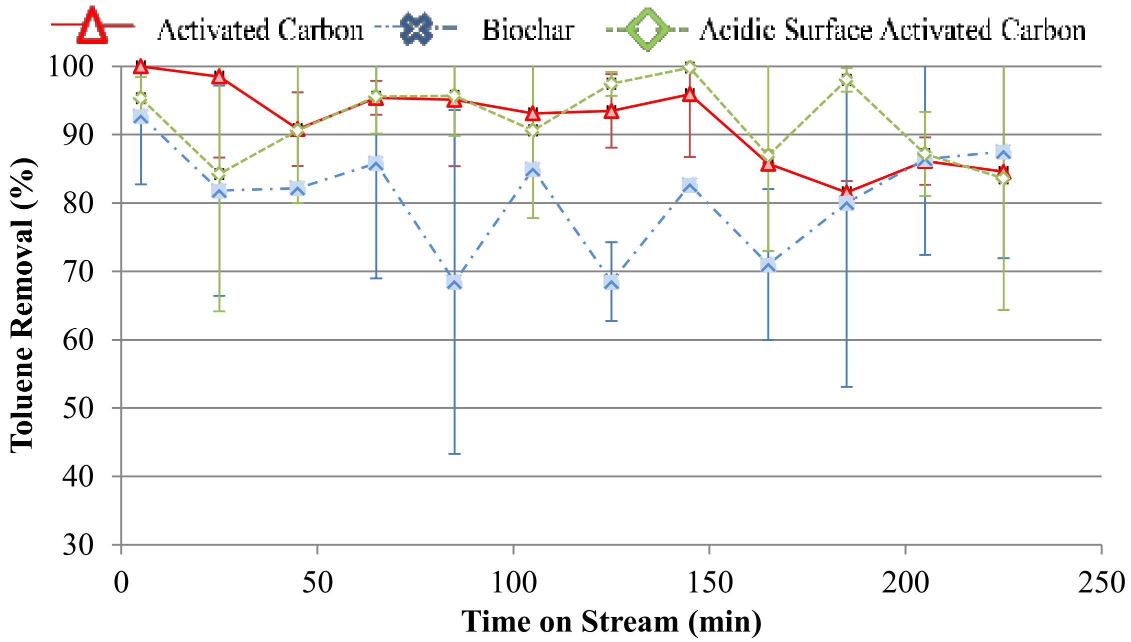


Fig. S8. Percent toluene removal vs. time on stream for activated carbon and biochar at 800 °C and nitrogen atmosphere. Experimental conditions were weight of activated carbon = 0.35 g, weight of char = 1 g, steam flow = 24 ml/hr, nitrogen flow = 1 scfh. Error bars represent standard deviation (2 replications for each data point).

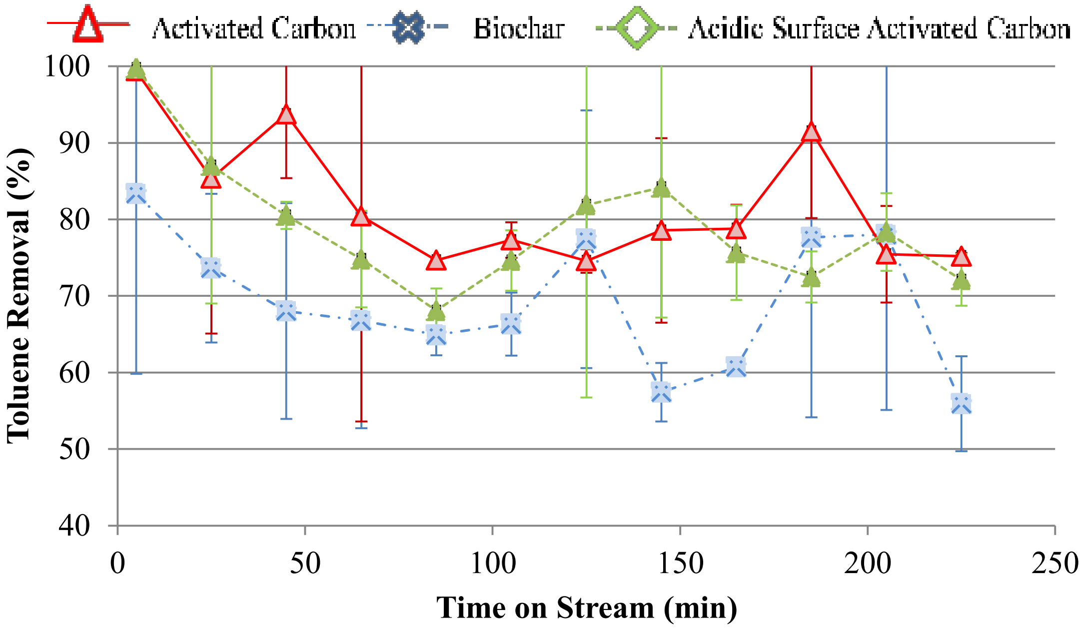


Fig. S9. Percent toluene removal vs. time on stream for activated carbon and biochar at 700 °C and producer gas atmosphere. Experimental conditions were weight of activated carbon = 0.35 g, weight of biochar = 1 g, producer gas flow = 1 scfh, steam to carbon ratio = 2. Error bars represent standard deviation (2 experiments for each data point).

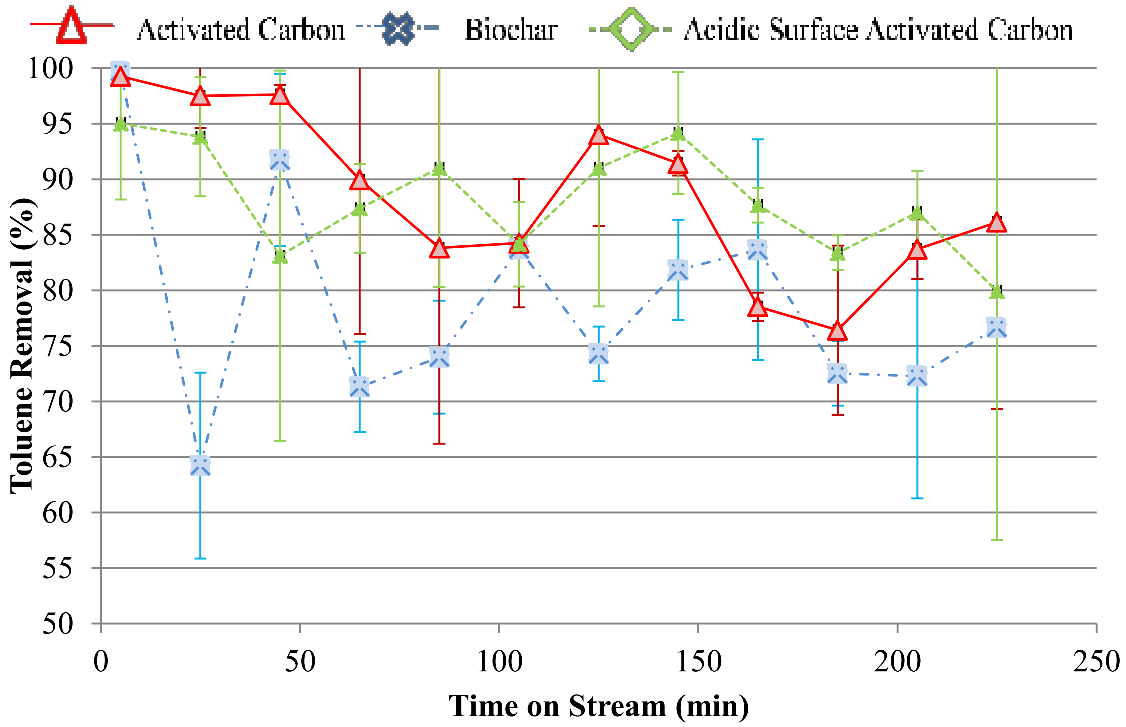


Fig. S10. Percent toluene removal vs. time on stream for activated carbons and biochar at 800 °C and producer gas atmosphere. Experimental conditions were weight of activated carbon = 0.35 g, weight of char = 1 g, producer gas flow = 1scfh, steam to carbon ratio = 2. Error bars represent standard deviation (2 experiments for each point).

Table S1: Proximate analysis of biochar and activated carbon derived from fluidized bed gasifier (FBG) and downdraft gasifier (DDG)

	FBG Biochar	FBG Activated Carbon	DDG Biochar	DDG Activated Carbon
Moisture % db[1]	2.07	18.14	2.36	6.84
Volatile Matter % db	0.64	2.00	1.53	0.95
Ash% db	78.26	1.21	21.25	1.07
Fixed Carbon %[2]	19.03	78.65	74.86	91.14

1: db - dry basis;

2: Fixed Carbon determined by difference between 100 and sum of the percent moisture, ash, and volatile matter

.

Table S2: Elemental analysis of biochar and activated carbon derived from fluidized bed gasifier (FBG) and downdraft gasifier (DDG)

		FBG biochar	DDG biochar	DDG Activated carbon	FBG Activated carbon
Total Nitrogen	% db[1]	0.05	0.69	0.82	0.69
Total Carbon	% db[1]	1.38	64.80	73.10	64.10
P	%	0.04	0.27	0.03	0.03
Ca	%	0.13	2.81	0.06	0.11
K	%	0.17	0.73	0.03	0.05
Mg	%	2.65	0.45	0.06	0.15
Na	%	0.03	0.13	0.01	0.01
S	%	0.01	0.04	0.01	0.01
Fe	%	0.78	0.29	0.04	0.09
Zn	ppm	79.4	97.8	4.7	5.9
Cu	ppm	5.7	8.8	2.8	2.6
Mn	ppm	130.1	394.5	12.8	71.3
Ni	ppm	303.7	4.6	1.3	1.8
Al	ppm	426.0	1408.0	80.2	675.3

[1] db = dry basis

Table S3: EDS spectra findings for fresh and used catalysts.

Elements (%wt)	Fresh Biochar	Used Biochar	Fresh Activated Carbon	Used Activated Carbon
Mg	0.5	0.77	0*	2.19
Si	82.55	63.57	56.68	45.58
K	13.84	13.74	13.69	4.66
Ca	3.11	11.6	29.63	27.83
Fe	0*	10.32	0*	14.43

Weight percent values are relative to total elements observed. 0*: Elements that are not identified

Table S4: Average gas concentration at outlet of the catalytic reactor at toluene flow rate of 2 ml/h and N_2 flow rate of 1 scfh, (average over time = 4 hours for 2 experiments)

Gas (% v/v)	Biochar		Activated Carbon		Acidic Surface Activated Carbon	
	700 °C	800 °C	700 °C	800 °C	700 °C	800 °C
CO	2.78	2.05	1.25	4.97	3.09	2.06
CO_2	0.07	0.28	0.29	0.99	0.70	0.33
H_2	2.10	1.67	1.92	8.66	4.50	1.67
CH_4	0.11	0.08	0.10	0.10	0.08	0.11

Table S5: Average gas concentration at the outlet of catalytic reactor at toluene flow rate = 2 ml/h and producer gas (5.15 % H_2, 7.49 % CH_4, 16.79 % CO_2, 19.30 % CO, and balance N_2) flow rate of 1 scfh (average over time = 4 hours for 2 experiments)

Gas (% v/v)	Biochar		Activated Carbon		Acidic Surface Activated Carbon	
	700 °C	800 °C	700 °C	800 °C	700 °C	800 °C
CO	15.64	17.55	19.7	19.9	19.6	19.29
CO_2	17.65	16.04	15.75	15.60	16.62	17.02
H_2	4.77	3.11	4.19	8.30	4.85	9.11
CH_4	6.29	6.65	5.52	5.57	6.78	6.25

CHAPTER IV

SIMULTANEOUS REMOVAL OF TOLUENE (MODEL TAR), NH_3, AND H_2S, FROM BIOMASS-GENERATED PRODUCER GAS USING BIOCHAR-BASED AND MIXED-METAL OXIDE CATALYSTS

Abstract

In this paper, effectiveness of four catalysts (biochar, activated carbon, acidic surface activated carbon, and mixed metal oxide) was studied for simultaneous removal of toluene, NH_3, and H_2S from biomass-generated producer gas. NH_3 (0.03 %), H_2S (0.015 %), and toluene at a flow rate of 2 ml/h were mixed with a synthetic producer gas composition (H_2: 8.5 %, N_2: 58 %, CO: 17 %, CH_4: 2 %, and CO_2: 11 %) and passed over a catalyst bed in a fixed-bed reactor tube maintained at 800 °C. Among the four catalysts, acidic surface activated carbon resulted in the highest toluene removal efficiency (97.5 %) and highest breakthrough time for NH_3 (145 min.). For H_2S removal, mixed metal oxides resulted in the highest breakthrough time (105 min.) among the four catalysts. Activated carbon showed good simultaneous removal capacity (91 % toluene removal efficiency; NH_3 adsorption capacity of 0.03g-NH_3/g-activated carbon; H_2S adsorption capacity of 0.008 g-H_2S/g-activated carbon) for the contaminants whereas biochar had moderate removal efficiencies (86 % toluene removal efficiency; NH_3 adsorption capacity of 0.008 g-NH_3/g-biochar; H_2S adsorption capacity of 0.008 g-H_2S/g-biochar). Results indicate that simultaneous removal of contaminants from producer gas is feasible using biochar-based catalysts. High

surface area mixed metal oxides synthesized using microwave and ultrasonication are also effective for simultaneous removal of contaminants.

1 Introduction

Biomass gasification shows increasingly great potential and much research is being conducted to advance this technology[1,2,3,4,5]. Various contaminants are present in producer gas generated from biomass gasification such as tars, ammonia (NH_3), and hydrogen sulfide (H_2S). The contaminants must be removed before the producer gas can be used in downstream applications for production of fuels, power, and chemicals[6,7,8]. Ammonia (NH_3) is formed primarily from the nitrogen containing compounds present in the biomass feedstocks. This fuel-bound nitrogen is released at high temperatures inside the gasifier. Ammonia is a precursor for NO_x emissions in downstream applications of the producer gas such as turbines, gas engines, and burners. NH_3 and other nitrogen containing compounds are also undesirable for catalytic upgrading and conversions as they poison catalysts. The ammonia content in producer gas has been found to vary between a few hundred ppm to 3% by volume[9]. Sulfur containing compounds such as carbonyl sulfide (COS) and hydrogen sulfide (H_2S) not only have a hazardous effect on health and the environment, but also lead to deactivation of downstream catalysts. Biomass consists of 0.1 % to 1% sulfur which results in H_2S volume concentration of 0.005 to 0.1 % in producer gas[10]. Tars (comprised of compounds having molecular weight higher than and including benzene) deactivate catalysts and clog process lines.

Various physical and chemical tar removal techniques such as scrubbers and electrostatic precipitators result in reducing the sensible heat content of the gas as the producer gas temperature, often greater than 350 °C at the exit of the gasifier,[1,2,3,4,5] decreases to around room temperature (25 °C) after contact with cold scrubbing solution[11]. Also, the disposal of the solvents used, as well as the high equipment and operation costs, make this process very uneconomical and inefficient[10,12]. On the contrary, catalysts offer a more cost efficient and equally effective approach to removal of these contaminants[13].

The type of catalyst to be used for gas cleaning depends on the nature of contaminants present in the gas. H_2S has an acidic character and hence, may interact with a suitable basic surface catalyst in an adsorption process. Chemical decomposition of ammonia using catalysts is not feasible due to high H_2 concentration in producer gas. Instead, researchers have proposed the use of high-surface-area acidic adsorbents to capture the NH_3 molecules[14,15] while mixed metal oxide and layered double hydroxide sorbents have shown promise for removal of sulfur containing compounds[16,17,18,19,20]. A catalyst which is capable of removing all the above mentioned contaminants simultaneously will reduce the number of unit operations necessary to condition the hot producer gas without loss in thermal efficiency. Catalyst regeneration capability, high removal efficiency for all the contaminants, effectiveness and sustained activity at high temperature, low cost, and easy disposal are the most desired properties of an ideal producer gas conditioning catalyst. A review of contaminants present in biomass gasification gas and effectiveness of various carbon-based catalysts for this removal can be found in Bhandari et. al.[21].

The majority of the research involving desulfurization of gas streams has focused on the use of solid metal-oxide sorbents. Single oxide sorbents have been employed previously and continue to be used [22]. However, these single oxides have several disadvantages such as low reactivity and inability to carry out deep desulfurization. Recently, research has focused on using mixed oxides rather than pure oxides[10,23,24]. Sulfided sorbents can also be regenerated by using steam. The overall scheme of sulfidation-regeneration chemistry in the presence of these mixed metal oxide sorbents is[10]:

$$MO + H_2S \rightarrow MS + H_2O$$

$$\mathrm{MS} + \frac{3}{2}\,\mathrm{O_2} \rightarrow \mathrm{MO} + \mathrm{SO_2}$$

where, MO and MS are metal oxide and metal sulfide respectively.

The process of simultaneous removal of gasification gas contaminants has been attempted. The removal of tars, NH_3, organic sulfur, and HCl using four different types of sorbents in combination with sixteen types of catalysts was carried out by Dou et. al.[25]. Nickel (Ni) catalysts were found to be the best for removal of NH_3 and tar while a combination of a self-prepared alkali and alkali earth metal sorbent and nickel catalyst had removal efficiencies above 88% for simultaneous removal of contaminants. A study on the activity of tar and ammonia over four different types of catalyst-dolomite, nickel, alumina, and SiC under different gas atmospheres in a fixed-bed tube reactor has also been conducted[26]. Dry reforming reactions are found to be more favorable than steam reforming reactions. Research over the years on coal gas desulfurization at Research Triangle Institute (RTI) shows a shift towards mixed metal oxides[13,15,27]. Researchers at RTI[13] developed a sorbent-catalyst combination of an NH_3 decomposition catalyst with a metal oxide sorbent for H_2S removal. The catalyst was synthesized using a co-precipitation technique. The catalyst was composed of zinc oxide for H_2S sorption and a combination of transition metals such as Ni, Co, Mo, and W, and supports such as TiO_2, Al_2O_3, and SiO_2 as catalyst for NH_3 decomposition. All of the 51 sorbent-catalyst combinations tested showed 99% H_2S removal efficiencies. The NH_3 removal efficiency was around 90% for the sorbent-catalysts and the efficiencies varied according to the type and level of the catalytic transition metals added. Various patents have focused on warm gas desulfurization using hydrotalcites as starting material[16,28]. Among the promising group of chemicals for adsorption and separation processes to stabilizers and catalysis are hydrotalcites. These are known as ionic clays or layered double hydroxides (LDH), with general formula of $M_x^{2+}M_y^{3+}(OH)_{2(x+y)}A_{y/n}^{-n}\cdot mH_2O$, where M^{2+} and M^{3+} are a divalent and a trivalent metal ions, respectively, and A^{-n} is an intercalated anion. Structurally, metal oxides or hydrotalcites are formed by brucite-like ($Mg(OH)_2$) sheets where isomorphous substitution of Mg^{2+} by a trivalent cation like Al^{3+} occurs. The positive charge of the layer is compensated by anions. The anion occupies the interlayer space along with water molecules[29,30]. Conventionally, co-precipitation technique is used to synthesize hydrotalcites. Co-precipitation involves addition of metal nitrates and precipitants at a fixed pH under stirring. The mixture of metal nitrates and precipitants is further subjected to ageing for prolonged time (6 to 69 h). Various modifications to this basic technique employ sonication, microwave, and techniques using different chemicals[30]. Calcination of hydrotalcites results in mixed oxides which are more active than hydrotalcite like ionic clay due to the presence of acido-basic pairs in their structure. The acido-basic properties are easily adjustable. Catalyst synthesis parameters such as calcination temperature, nature, and ratio of divalent to trivalent cations, and the crystalline size affect the nature of acidic and basic sites in the mixed oxides[31].

XRD images from a study on the effectiveness of hydrotalcite in hydrodesulfurization (HDS) of gasoline indicate that the Zn–Al hydrotalcite has more uniform crystal and bigger crystal size than those of Mg–Al and Cu–Al hydrotalcites. Zn-Al hydrotalcites were shown to increase the selectivity of catalysts for hydrodesulfurization of sulfur-containing compounds during hydrogenation of olefins. Zhao et al.[17] obtained 75-85% hydrodesulfurization efficiency for Zn-Al, Mg-Al, and Cu-Al hydrotalcites. Calcined layered mixed hydroxides (hydrotalcite type anionic clays) have been used previously for SOx removal[32]. Various sorbents used for high temperature desulfurization are mixed-metal oxides fabricated from ZnO, FeO, TiO_2 or a combination of the three with other organic and inorganic binders and metal oxides.

In the presence of ammonia, better removal of hydrogen sulfide is obtained due to ammonia decomposition. Up to 89% NH_3 removal after 8 activations of ZnO/TiO_2 along with bentonite and molybdenum oxide as a base mixture has been observed[16]. The reaction pathway is shown below.

$$\mathrm{MoO_3} + 2\mathrm{H_2S} + \mathrm{H_2} \rightarrow \mathrm{MoS_2} + 3\mathrm{H_2O}$$

$$\mathrm{NH_3} \rightarrow \mathrm{H_2} + \mathrm{N_2} \ \text{(in presence of Mo)}$$

In another study, two calcined layered double hydroxides (LDHs) of Mg-Al were evaluated for H_2S and COS adsorption. The catalysts were evaluated in a simulated set up for catalysis. The catalysts were operated at 25 °C and both showed significant adsorption efficiencies for H_2S and COS. One of the mechanisms proposed for H_2S adsorption is dissociation as shown below[16]:

$$H_2S + 2M - O - M \rightarrow M - SH + M - OH$$

Also, another route plausible is through reaction of H_2S with a defective site or oxygen vacancy along with the formation of H_2O as shown below[16]:

$$H_2S_{ads} + M^{n+}O^{2-} + OH^- \rightarrow (H_2O)_{ads} + OH^- + Mn^+S^{2-}$$

In the case of MgO, S^{2-} is directly incorporated into the surface of MgO due to its basicity:

$$H_2S + Mg - O - Mg \rightarrow H_2O + Mg - S - Mg$$

In a study carried out to remove CO_2 and H_2S in a co-adsorption process, a K_2CO_3 promoted Mg-Al hydrotalcite based material has shown promise[19].

Activated carbon is a promising catalyst for sulfur adsorption and its low cost and simpler synthesis offers an added advantage. It is suggested that the choice of a sulfur sorbent be made based on acidity of the sorbent and associated parameters such as number of acidic groups, surface pH, and amount of surface oxygen groups[31]. The reaction mechanism of H_2S adsorption on the carbon surfaces can be summarized into the following three types of reactions:

$$C + H_2S \rightarrow CS + H_2O$$

$$CO + H_2S \rightarrow CS + H_2$$

$$CM + H_2S \rightarrow CMS + H_2$$

Ammonia removal over carbon-based catalysts has also been studied previously[33]. Ammonia removal using catalysts or sorbents is thought to proceed through one of the following two reaction mechanisms[10]:

$$2NH_3 \rightarrow N_2 + 3H_2$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

The objectives of this study were a) evaluate a novel technique for synthesis for mixed metal oxide catalyst, using microwave and ultrasound, and c) evaluate the effectiveness of four synthesized catalysts (biochar, activated carbon, acidic surface activated carbon, and mixed metal oxide) for simultaneous removal of tars, ammonia, and H_2S in a fixed-bed reactor.

2 Experimental

2.1 Catalyst synthesis

Mixed metal oxide catalysts were synthesized using microwave and ultrasound. Metal nitrate mixtures at a molar ratio M^{2+}:Al^{3+} of 2:1 were dissolved in water (M being any metal, in this experiment, zinc). Urea solution corresponding to Urea/(M^{2+} + Al) molar ratio of two was added to the mixture and microwaved at 100% power for 30 min. followed by ultrasonication using a sonication probe. Ultrasonication was performed on the mixture using a probe type sonicator (Fisher Scientific 550 sonic disembrator, Pittsburgh, PA) to improve surface area and dispersion of particles. Sonication was performed for 30 min. at 30 % power to ensure sufficient time for crystallization of hydrotalcites. Hydrolysis of urea will provide the alkaline conditions required for the reaction. The mixture was placed in an oven at 80 °C for 3 h followed by filtration and drying of the precipitate. Filtered cake was dried in an oven at 110 °C for 24 h. The hydrotalcite cake was then mixed with 1% nitric acid which was dried at 110 °C for 3 h and calcined at 450 °C in furnace for 4 h.

Biochar was generated in a downdraft gasifier and fluidized bed gasifier using switchgrass as the feedstock. The details of the gasifier have been described elsewhere[4,5]. The procedure for the synthesis of the activated carbon is based upon a previous study by Azargohar and Dalai (2006) with some modifications[34] and has been described previously[35]. Activated carbon was coated with 1 % dilute citric acid followed by drying at 100 °C to give acidic surface activated carbon. The synthesized metal oxide catalysts were characterized using scanning electron microscopy, fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA).

2.2 Surface area and porosity measurements

The Brunauer-Emmett-Teller (BET) method was used to determine the surface area of the catalysts. Barrett, Joyner, and Halenda (BJH) and Dollimore and Heal (DH) techniques were also used for catalyst surface and pore characterization. Characterization was carried out using Quantachrome surface area analyzer (Autosorb 1-C, Quantachrome, Boynton Beach, FL). Decreases in surface area, pore radius, and pore volume were calculated using the formula:

$$\text{Decrease (\%)} = \frac{\text{Original Value} - \text{Final Value}}{\text{Original Value}} \times 100$$

where, original and final values are surface areas (m^2/g), pore radii (A°), and pore volumes (cc/g) of fresh and used catalysts, respectively.

2.3 Simultaneous removal of contaminants

Fixed bed reactor experiments were performed in a stainless steel reactor tube (diameter = 0.01m, length = 0.9m) as shown in Fig. 1. The tube was heated in a high temperature reactor jacket (Carbolite Inc). The gas inlet and exit lines of the reactor were made of 0.0006 m inner diameter stainless steel tubes (Swagelok, Tulsa, OK). All the lines were maintained at 250 °C using heat tapes (Omega Engineering, Stamford, CT). The catalyst was supported by quartz wool inside the stainless steel reactor tube (McMaster Carr) at a height of 0.6 m from the top of the tube which was the constant temperature zone of the reactor. Toluene and ammonium sulfide were introduced from two separate syringe pumps (Hamilton Inc., Reno, NV) into the reactor and mixed with a producer gas composition controlled from a cylinder. Ammonium sulfide solution (Fisher Scientific Inc.) with volume concentration of 0.35 % was injected at the rate of 2.1 ml/h into the reactor. After decomposition at high temperature, ammonium sulfide dissociates to yield approximately ammonia volume concentration of 0.03 % and H_2S volume concentration of 0.015 %. All the gas cylinders used-both for calibration of equipment as well as for experiments-were purchased from Stillwater Steel Inc. (Stillwater, OK). The molar gas composition prepared was as follows: H_2 5.126 %, CO_2 16.78 %, CO 19.25 %, CH_4 7.489 %, H_2S 0.015 %, NH_3 0.03 %. Producer gas flow rate was controlled using a calibrated rotameter (Airgas, Tulsa, OK). Gas was collected at the exit of the reactor in syringes and gas bags. The gases were analyzed using a gas chromatograph (Agilent 7890 Series II, Agilent Technologies, Santa Clara, CA) and mass spectrometer (5975C, Agilent Technologies, Santa Clara, CA) equipped with a real-time gas analyzer (Diablo Analytical Inc., Antioch, CA). The experimental conditions were temperatures of 800 °C, gas residence time approximately 0.03-0.1 $kg \cdot m^3 \cdot h^{-1}$ and test time of 4 h. Gas residence time, τ ($kg \cdot m^3 \cdot h^{-1}$) was defined as,

$$\tau = \frac{w}{v_0}$$

where, w is the weight of the catalyst (kg) and v_o is the flow rate of the gas mixture at the catalyst bed (m^3/h). Different catalyst quantities were used to ensure same bed height (0.014 m) and bed volume (4.39×10^{-8} m^3) for all the experiments. The quantities of catalysts evaluated were 1 g biochar and 0.35 g each of activated carbon, acidic surface activated carbon, and mixed metal oxide. Toluene removal efficiency was defined as

$$X=100 \times \frac{(Cin- Cout)}{Cin}$$

where, X is the percent removal of toluene, and C_{in} and C_{out} are the concentrations of toluene (volume %) at the inlet and outlet, respectively. For evaluation of ammonia and H_2S removal, time taken for saturation of catalyst bed or 'breakthrough time' is defined as time at which C_{out}/C_{in} is 1. Adsorption capacity of NH_3 and H_2S of the catalysts (M_{ads}) was calculated assuming standard temperature and pressure (STP; 0 °C, 1 atm) conditions using the following equation:

$$\mathrm{M_{ads}} = \frac{\text{Quantity of contaminant adsorbed (g)}}{\text{Unit Weight of catalyst (g)}}$$

2.4 Statistical analysis

Statistical analysis of the data was carried out with the help of SAS 9.3 (Carey, NC) statistical software. Post-hoc multiple comparisons were performed for BET surface area of hydrotalcite catalysts, toluene removal efficiency, and NH_3 and H_2S adsorption capacities, using LSD and Duncan's tests (α = 5 %). Correlations among the variables were also evaluated (α = 5 %).

3 Results and discussion

3.1 Effect of microwave and ultrasound on synthesis of mixed metal oxide

BET surface area (Table 1) was significantly higher for mixed metal oxide synthesized using both microwave and ultrasound than only microwave or only ultrasound. Upon increasing the microwave time by 5 min. from the original 5 min., a significant increase in surface area of the resulting metal oxide was observed. Ultrasonication for 30 min. also reduced formation of agglomerates. Combined microwave and ultrasound treatment resulted in homogeneously shaped particles as seen from scanning electron microscopy images (Fig. 2). From the FT-IR images (Fig. 3), hydrotalcite structure was identified and presence of nitrates and carbonates were also confirmed[36,29,30,37]. Thus, a novel technique employing combined microwave irradiation and ultrasonication treatment has shown improved particle porosity and surface area.

3.2 Surface Area

Surface areas of fresh and used catalysts are shown in Table 2. Among the four catalysts evaluated, surface area for fresh catalysts was highest of fresh activated carbon (703.3 m^2/g) whereas lowest was that of fresh biochar (16.7 m^2/g). For original biochar catalyst, a significant decrease in BET surface area (68 %) and Langmuir surface area (69 %) was observed. For activated carbon, marginal decreases in BET surface area (1%) and Langmuir surface area (2%) in the used catalysts were observed, which were not found to be significant. The marginal decrease in surface area (1 % to 2 %) in used activated carbon compared to fresh activated carbon possibly indicates that in the fixed-bed reactions, surface area of activated carbon does not play the primary role and removal of contaminants takes place possibly by use of pores of the activated carbon. The decrease in surface areas (Langmuir and BET surface area) for the acidic surface activated carbon catalysts was not significant (about 10 %) whereas the same for mixed metal oxide was significant (about 68 %). The desorption surface area calculated using the BJH method and DH method evaluates desorption surface area of catalyst independent of external area due to sample particle size. Desorption surface areas were significantly higher of all the fresh catalysts than those of used catalysts (26 to 62 % higher) except that of acidic surface activated carbon (decrease of 43 %). The significantly higher desorption surface area of used acidic surface activated carbon (79.3 m^2/g) than the corresponding fresh catalyst (55.6 m^2/g) indicates that more gas is desorbed from the used catalyst as compared to fresh catalyst due to large adsorption taking place on the catalyst surface during the reactions. The better performance (97 % toluene removal efficiency; NH_3 breakthrough time 45 min.; H_2S breakthrough time 70 min.) of acidic surface activated carbon can be inferred from the higher desorption surface area. The t-method external surface area of the catalysts is significantly higher for fresh activated carbon (265 m^2/g) as compared to that of acidic surface activated carbon (121 m^2/g). This indicates that there is a decrease in external surface area during the process of coating the activated carbon with dilute acid. For fresh mixed metal oxide catalyst, the external surface area (177 m^2/g) as well as BET (182 m^2/g) and Langmuir surface areas (357 m^2/g) were found to be very high indicating that ultrasonication contributed to development of pores and improved surface area. The decrease in t-method micropore area of activated carbon (0.5 % decrease) was not significant indicating that activated carbon micropores did not play a major role in removal of contaminants. The decrease in micropore area in used catalysts as compared to fresh catalysts was significantly higher for the other three catalysts (mixed metal oxide (79 %), acidic surface activated carbon (20 %), and biochar (~82 %). The trend seems to indicate that micropores of these catalysts get saturated during the reactions.

3.3 Pore volume

Table 3 shows the pore volume data of both fresh and used catalysts. As expected, the total pore volume (pores with radius less than 13.4 A°) for both the fresh activated carbons was significantly higher (about 0.4 cc/g) compared to that of fresh biochar and fresh mixed metal oxide (0.01 - 0.1 cc/g). The high pore volume in the low pore diameter range for the activated carbons is possibly due to large number of micropores present. Desorption pore volumes for biochar catalysts were significantly lower than the other three catalysts (activated carbons and mixed metal oxide).

3.4 Pore size

The average pore radii (Table 4) of all the catalysts were in the range of 10-11 A°. A marginal decrease in pore radii (1 to 5 %) was observed in all the catalysts after use. The desorption pore radii were in the 9.8-11 A° range of biochar and activated carbons. The DR method micropore radii for both fresh and used mixed metal oxide catalysts (25 to 26 A°) were significantly higher than the other catalysts ($\alpha = 5$ %).

3.5 Contaminant removal efficiency and gas concentrations

3.5.1 Toluene removal

In our previous work[35], we reported toluene removal efficiencies of around 78.8%, 88.5%, and 88.1% for biochar, activated carbon, and acidic surface activated carbon respectively, at a temperature of 800 °C. These experiments were carried out to evaluate toluene removal efficiencies without the addition of ammonia or H_2S. In this study, in the presence of ammonia and H_2S, toluene removal efficiency (Table 5) was significantly higher for acidic surface activated carbon (97.56%) compared to other three catalysts (biochar, activated carbon, and mixed metal oxide). The average toluene removal efficiencies for activated carbon, biochar, and mixed metal oxide obtained were 91.60%, 86.69% and 83.66% respectively. Thus, the toluene removal efficiency was higher for all the biochar-based catalysts (biochar, activated carbon, and acidic surface activated carbon) in the presence of ammonia and H_2S than without them. This increase in toluene removal efficiencies indicates that ammonia and H_2S play a role in improving the toluene removal efficiencies. No published results were found for high temperature reactions of ammonia, H_2S and toluene. In a study carried out by Masuda et. al.[38], the influence of various gases on H_2S removal efficiency was measured. They found that removal ratio of H_2S improved in the presence of ammonia; whereas the same decreased in the presence of toluene. However, ammoxidation reactions such as that shown below occur in the presence of O_2 or an oxidative catalyst[39]. Ammoxidation type of reactions may have occurred over the catalysts evaluated in this study, especially over metal oxide catalysts.

$$\mathrm{C_6H_{12}CH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow C_6H_{12}CN + 3\ H_2O}$$

Producer gas is reducing in nature due to high hydrogen content and absence of oxygen. Hydrogen sulfide adsorbs strongly onto $NiMo/Al_2O_3$ catalyst in the presence of ammonia and inhibits toluene hydrogenation[40]. Thus, although the available literature indicates that hydrogen sulfide and ammonia have a detrimental effect on toluene removal when reacted separately or simultaneously with different reaction conditions than used in this study, simultaneous presence of all three compounds i.e. toluene, ammonia, and H_2S, results in better toluene removal efficiencies for the catalysts evaluated at a temperature of 800 °C. From the plot of toluene removal efficiency vs. time on stream (Fig. 4), it can be observed that removal efficiency did not decrease significantly ($p = 0.6$) by the end of the four-hour evaluation time for acidic surface activated carbon. The removal efficiency for biochar started to decrease significantly ($\alpha = 1$ %) from approximately 80 min. time on stream possibly due to coking and attrition of the catalyst. Although a decrease in removal efficiency over time was observed for all of the catalysts, the decrease was not significant for activated carbons and mixed-metal oxide catalysts.

3.5.2 Ammonia removal

Breakthrough curves for ammonia (Fig. 5) indicate that catalyst bed saturation takes place fastest for original biochar catalyst (NH_3 breakthrough time around 100 min.). Removal of contaminants on biochar catalyst is thought to take place through surface and micropore filling as discussed above in section 3.5.1 and 3.5.2. The time taken for saturation of the catalyst bed by ammonia or breakthrough time of mixed metal oxide and activated carbon was lower (about 120 min.) compared to acidic surface activated carbon (about 170 min.). Also, C/C_0 is much lower for acidic surface activated carbon for a longer time compared to that for the other catalysts indicating that acidic surface contributes to higher ammonia removal efficiency. The high breakthrough time also indicates that acidic surface of the activated carbon maintains catalytic activity of the catalyst for a longer time. Activated carbon, acidic surface activated carbon, and mixed metal oxide had an adsorption capacity of NH_3 of around 0.03 g-NH_3/g-catalyst which was significantly higher than that for biochar (0.008 g-NH_3/g-biochar).

3.5.3 H_2S removal

Breakthrough curves for H_2S (Fig. 6) highlight that mixed metal oxide performed the best for H_2S removal (M_{ads} = 0.01 g-H_2S/g-catalyst). The breakthrough time obtained for mixed metal oxide was around 100 min.; whereas, the breakthrough time for the other three catalysts was around 70 min. All the other three catalysts, i.e. biochar, activated carbon, and acidic surface activated carbon, performed equally well for H_2S removal (M_{ads} = 0.008 g-H_2S/g-catalyst). Significant decreases in BET surface area, total pore volume, as well as micropore volume of mixed metal oxide catalyst were observed after use which possibly indicates that removal of H_2S over metal oxide catalysts proceeds via vast utilization of the surface of the metal oxide. Thus, a larger surface area of the metal oxide might aid in removal of contaminants. Therefore, preliminary evaluation carried out in this work combining microwave and ultrasound treatment for synthesis of metal oxide catalysts is promising for further research towards large-scale commercial synthesis of these catalysts. The H_2S adsorption capacity for mixed metal oxide catalyst (around 0.01 g-H_2S/g-mixed metal oxide) was significantly higher than that for biochar, activated carbon, and acidic surface activated carbon (around 0.008 g-H_2S/g-catalyst).

4 Conclusion

Mixed-metal oxide catalysts were successfully synthesized using microwave and ultrasound. Combined microwave and ultrasound synthesis of mixed metal oxide resulted in significantly higher surface area catalysts than individual microwave or ultrasound treatment. The experimental evaluation of simultaneous removal of three common biomass gasification producer gas contaminants, i.e. tars, ammonia, and H_2S, over four catalysts, i.e. biochar, activated carbon, acidic surface activated carbon, and mixed metal oxide, was studied. For removal of toluene, activated carbon catalysts performed significantly better (92-98 %) than biochar (87 %) or mixed metal oxide (84 %). Ammonia adsorption capacities for activated carbons and mixed metal oxide catalysts were significantly higher than that of biochar; whereas mixed metal oxide had significantly higher H_2S adsorption capacity than the other three catalysts. The toluene removal efficiencies measured during simultaneous removal of contaminants was much higher (3 to 8 % higher toluene removal efficiencies) than that for only toluene removal (previous study[35]) which indicated that simultaneous presence of contaminants aids removal of toluene. The results also indicated that the carbon-based catalysts (biochar and activated carbons) had good efficiency for simultaneous removal of contaminants (86 to 97 % toluene removal efficiency; NH_3 breakthrough time of 90 to 150 min.; H_2S breakthrough time of 80 to 110 min.). Higher surface area and larger pore volume of catalysts contributed to removal of contaminants. Inexpensive carbon-based catalysts evaluated in this study combined with good removal efficiencies of contaminants add to the potential benefits in gas cleanup. Finally, series of carbon catalyst beds and metal oxide beds or metal oxide catalysts loaded onto high surface area carbon supports can decrease the number of stages required for gas cleanup and thus reduce capital costs.

Acknowledgments

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Figures:

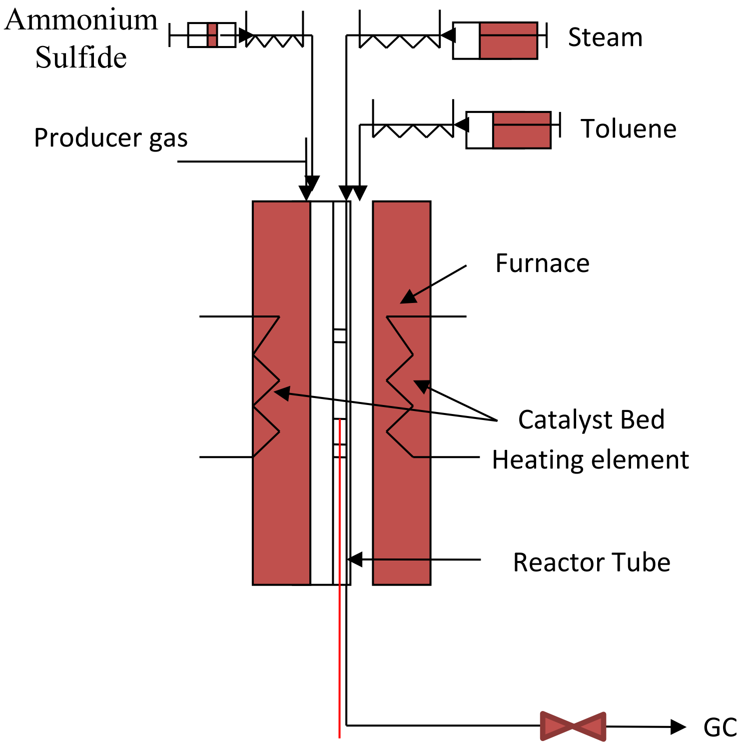

Fig. 1: Process schematic of fixed bed reactor

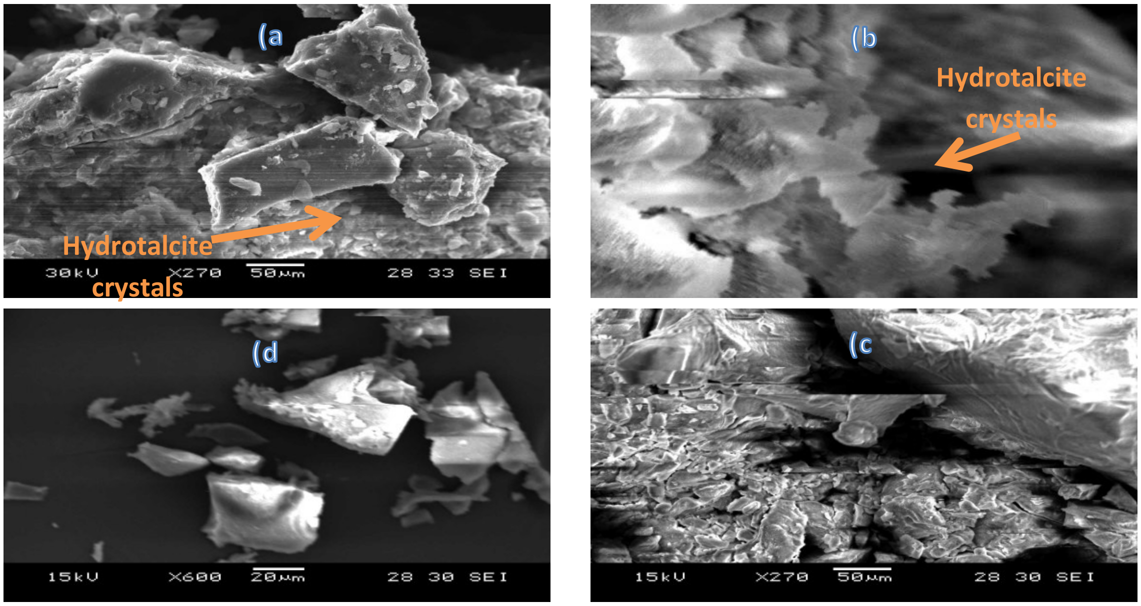

Fig. 2: Scanning electron microscopy images of Zn-Al hydrotalcite (clockwise from left top): (a) 5 min. microwave with ultrasonication; (b) 10 min. microwave with ultrasonication; (c) only ultrasonication; (d) only 5 min. microwave.

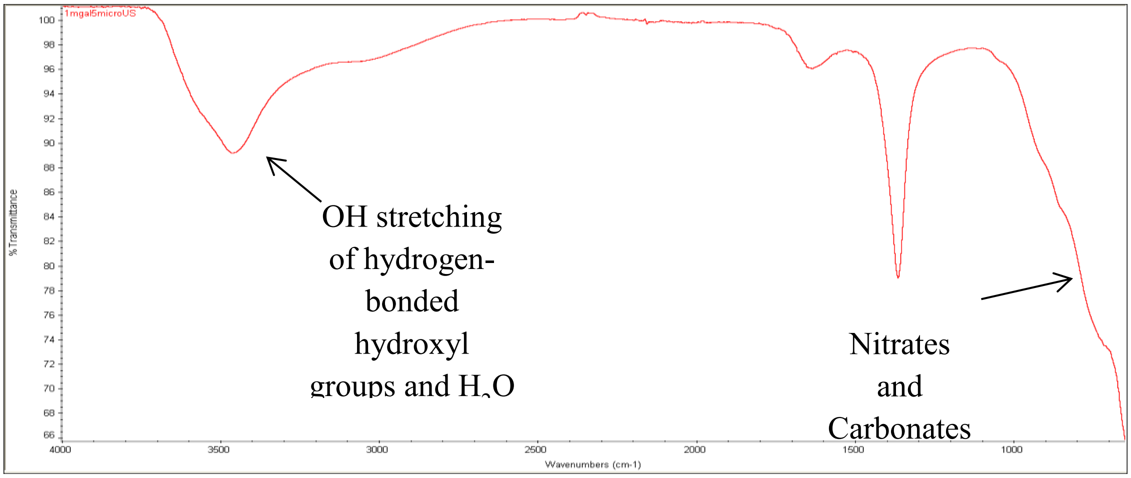

Fig. 3: Representative FT-IR spectrum of Zn-Al hydrotalcite (sample conditions: 5 min. microwave)

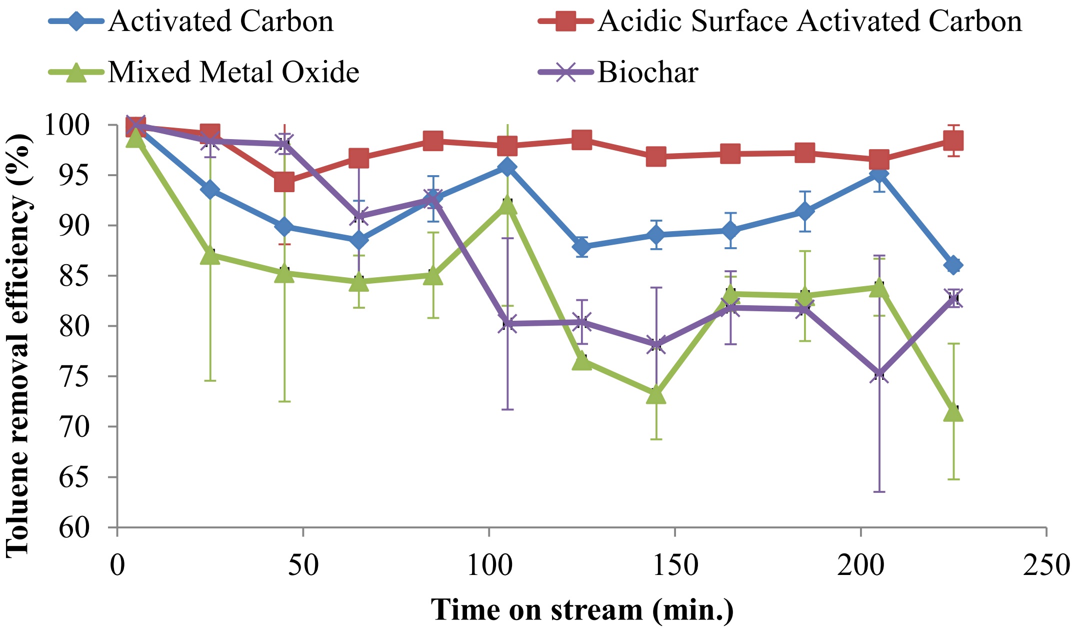

Fig. 4: Toluene removal efficiency with time for tested catalysts. (Reactor temperature = 800 °C, gas residence time = 0.03-0.1 kg·m^3·h^{-1} , catalyst quantities: 1 g biochar, 0.35 g each of activated carbon, acidic surface activated carbon, and mixed metal oxide)

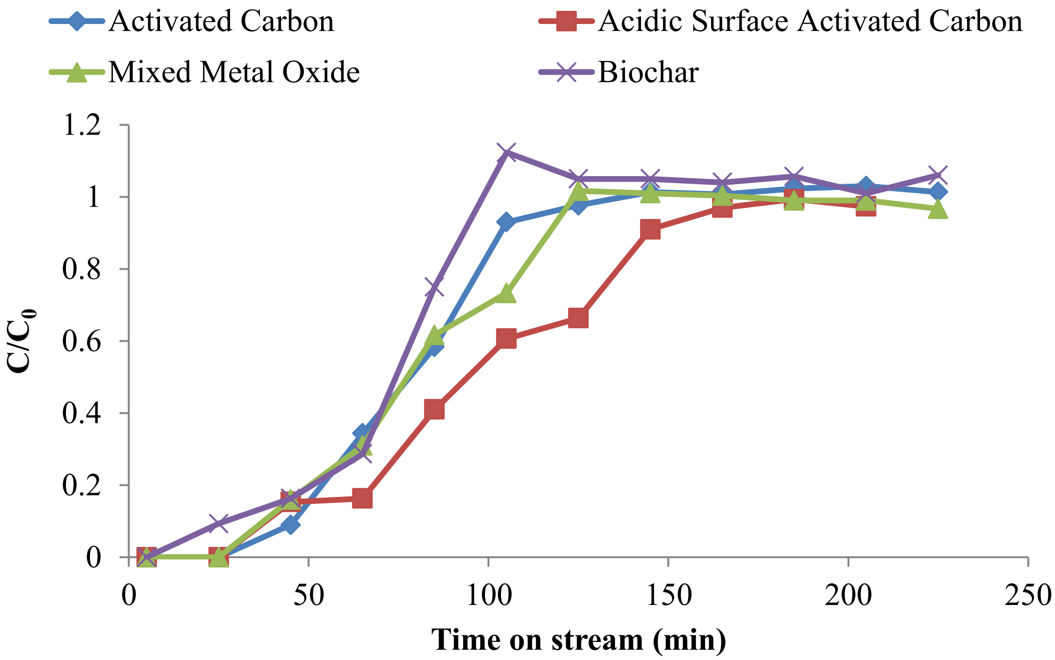

Fig. 5: Breakthrough curve for ammonia with time on stream (C/C_0: ratio of final outlet ammonia concentration (ppm) to inlet ammonia concentration (ppm), reactor temperature = 800 °C, gas residence time = 0.03-0.1 $kg{\cdot}m^3{\cdot}h^{-1}$, catalyst quantities: 1 g biochar, 0.35 g each of activated carbon, acidic surface activated carbon, and mixed metal oxide)

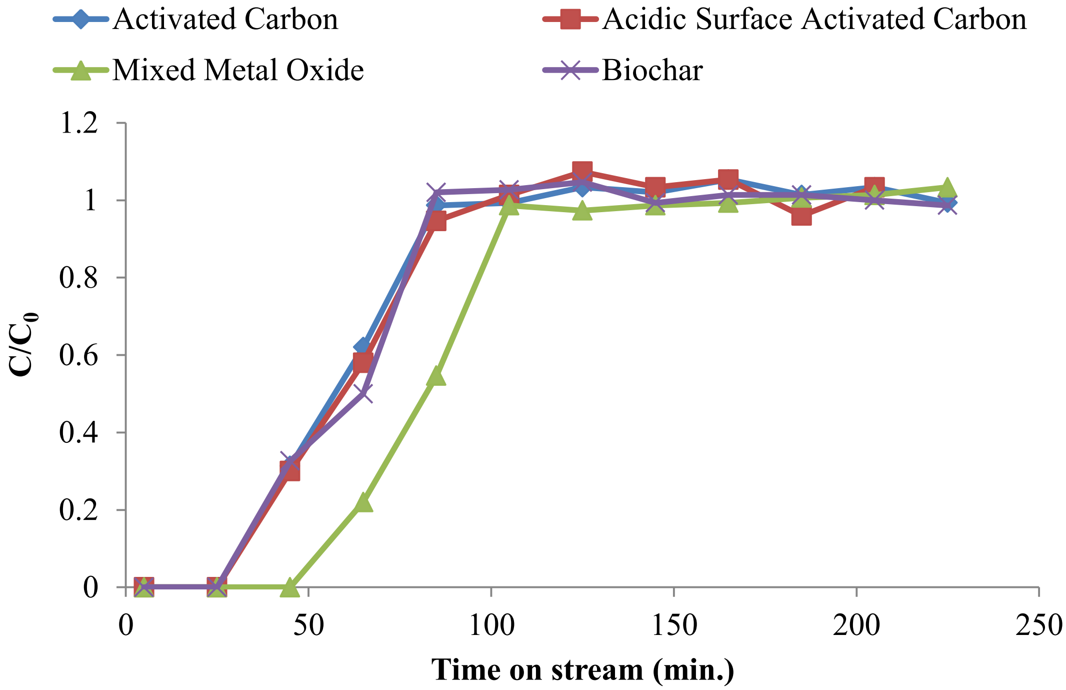

Fig. 6: Breakthrough curve for H_2S with time on stream (C/C_0: ratio of final outlet H_2S concentration (ppm) to inlet H_2S concentration (ppm), reactor temperature = 800 °C, gas residence time = 0.03-0.1 $kg{\cdot}m^3{\cdot}h^{-1}$, catalyst quantities: 1 g biochar, 0.35 g each of activated carbon, acidic surface activated carbon, and mixed metal oxide)

Table 1: BET surface area of hydrotalcite catalysts synthesized (ultrasonication time = 30 min.)

Synthesis technique	BET Surface Area (m^2/g)
5 min. microwave	130.81^c
5 min. microwave + ultrasonication	200.45^a
10 min. microwave + ultrasonication	188.89^b
Ultrasonication only	64.41^d

*Means followed by same letter are not significantly different ($\alpha = 5$ %)

Table 2: Surface area (m^2/g) of fresh and used catalysts

Surface area method	Biochar		Activated carbon		Acidic surface activated carbon		Mixed metal oxide	
	Fresh (m^2/g)	Used (m^2/g)	Fresh (m^2/g)	Used (m^2/g)	Fresh (m^2/g)	Used (m^2/g)	Fresh (m^2/g)	Used (m^2/g)
Multipoint BET[1]	16.73^{e}	6.244^{f}	703.3^{a}	695.5^{a}	697.1^{a}	634.0^{b}	182.8^{c}	57.87^{d}
Single Point BET[1]	18.24^{e}	6.51^{f}	762^{a}	770.3^{a}	772.1^{a}	694.3^{b}	182.5^{c}	57.42^{d}
Langmuir	27.4^{e}	10.76^{f}	1193^{a}	1162^{a}	1165^{a}	1045^{b}	357.2^{c}	109.3^{d}
BJH[2] Cumulative Desorption	1.947^{f}	1.403^{g}	118.2^{a}	55.48^{ab}	55.6^{b}	79.27^{c}	64.40^{d}	24.53^{e}
DH[3] Cumulative Desorption	2.18^{f}	1.45^{g}	122.9^{a}	57.75^{d}	57.88^{d}	82.49^{b}	66.52^{c}	25.45^{e}
t-Method External	3.29^{e}	3.84^{e}	265.3^{a}	121^{c}	121.2^{c}	176.3^{b}	177.4^{b}	56.73^{d}
t-Method Micro Pore	13.44^{d}	2.4^{ef}	438^{c}	574.5^{a}	575.8^{a}	457.7^{b}	5.40^{e}	1.14^{f}
DR[4] Micro Pore	27.17^{g}	10.01^{h}	1153^{a}	1147^{c}	1149^{b}	102.2^{e}	305.0^{d}	94.18^{f}

[1]BET-Braun, Emmett, and Teller; [2]BJH-Barrett, Joyner & Halenda; [3]DH-Dollimore & Heal;

[4]DR-Dubinin-Radushkevich

*Means followed by same letter within a row are not significantly different (α = 5 %)

Table 3: Pore volume of fresh and used catalysts

Pore Volume Method	Biochar		Activated carbon		Acidic surface activated carbon		Mixed metal oxide	
	Fresh (cc/g)	Used (cc/g)	Fresh (cc/g)	Used (cc/g)	Fresh (cc/g)	Used (cc/g)	Fresh (cc/g)	Used (cc/g)
Total Pore Volume for pores with Radius less than 13.4 A° at P/P_0 = 0.31475	0.009^{f}	0.003^{g}	0.393^{b}	0.401^{a}	0.401^{a}	0.352^{c}	0.094^{d}	0.03^{e}
BJH[1] Cumulative Desorption	0.001^{f}	0.001^{f}	0.065^{a}	0.031^{d}	0.031^{d}	0.043^{b}	0.037^{c}	0.014^{e}
BJH[1] Interpolated Cumulative Desorption (Pore Radius = 0 to 5000 A°)	0	0	0	0	0	0	0	0
DH[2] Cumulative Desorption	0.001^{f}	0.001^{f}	0.065^{a}	0.03^{d}	0.03^{d}	0.043^{b}	0.036^{c}	0.014^{e}
t-Method Micro	0.008^{c}	0.001^{c}	0.259^{b}	0.339^{a}	0.34^{a}	0.265^{b}	0.004^{c}	0.001^{c}
DR[3] Micro	0.001^{e}	0.004^{e}	0.411^{a}	0.409^{a}	0.41^{a}	0.364^{b}	0.109^{c}	0.034^{d}

[1]*BJH-Barrett, Joyner & Halenda;* [2]*DH-Dollimore & Heal;* [3]*DR-Dubinin-Radushkevich*

*Means followed by same letter within a row are not significantly different (α = 5 %)

Table 4: Pore size for evaluated catalysts

Pore Radius Method	Biochar		Activated Carbon		Acidic Surface Activated Carbon		Mixed Metal Oxide	
	Fresh (°A)	Used (°A)	Fresh (°A)	Used (°A)	Fresh (°A)	Used (°A)	Fresh (°A)	Used (°A)
BJH[1] Desorption	10.82	11.90	9.86	9.81	9.93	9.78	10.38	12.82
DH[2] Desorption	10.82	11.90	9.86	9.81	9.93	9.78	10.38	12.82
DR[3] Micro Pore Width/2	10.35	18.35	14.46	10.11	9.75	12.14	26.03	25.11
Average	11.19	10.61	11.18	11.5	11.52	11.12	10.28	10.18

[1]BJH-Barrett, Joyner & Halenda; [2]DH-Dollimore & Heal; [3]DR-Dubinin-Radushkevich

Table 5: Toluene removal efficiencies of biochar, activated carbon, acidic surface activated carbon and mixed metal oxide.

Catalyst	Toluene removal efficiency (%)
Biochar	$86.69^{c} \pm 3.59$
Activated carbon	$91.60^{b} \pm 1.29$
Acidic surface activated carbon	$97.56^{a} \pm 0.99$
Mixed metal oxide	$83.66^{c} \pm 5.27$

*Means followed by same letter are not significantly different (α = 5 %)

VITA

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