Full Length Article

Assessing tar removal in biomass gasification by steam reforming over a commercial automotive catalyst

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ABSTRACT

Biomass gasification is a primary thermochemical conversion technology for transforming woody biomass feedstocks into a range of renewable fuels and chemicals. However in practice during biomass gasification, tar formation is practically unavoidable and tar removal during downstream synthesis gas cleaning is crucial to achieving high-quality synthesis gas at commercial scale. A category of catalytic tar reforming (tar cracking) catalysts typically utilizes precious metals including rhodium, which shows high reactivity toward gasification tar, resists coking and is more tolerant to sulphur compared to nickel. As such, they are similar to automotive exhaust after-treatment catalysts. In this study we evaluated how a commercial automotive catalyst performed as a gasification tar reforming catalyst. We tested the catalyst at bench scale for methanol reforming and tar reforming at 700 °C using 80/20 mixtures of methanol/water, and 79.5/20/0.5 mixtures of methanol/water/tar and methanol/water/guaiacol in flowing nitrogen.

Methanol was 95% converted to synthesis gas at 700 °C and the catalyst did not deactivate during 48 h on stream. Methanol/water mixtures containing 4925 ppm gasification tar also reacted readily over the catalyst to produce syngas, but catalyst deactivation occurred over tens of hours of continuous operation, indicated by decreased conversion of the methanol/tar feed. The catalyst was regenerated by calcining in air at 500 °C, which allowed catalyst to operate for 120 h. Methanol/water/guaiacol mixtures also reacted readily to produce syngas, but as with tar, the catalyst deactivated over tens of hours continuous operation with methanol/guaiacol feed. SEM data confirmed that coking of the catalyst was the likely cause of deactivation. At relatively high reaction temperature and contact times of seconds used in this study, guaiacol was completely deoxygenated, but a fraction of the guaiacol was methylated over the catalyst to form methyl-substituted benzenes, toluenes and xylenes (BTX).

1. Introduction

Biomass gasification is regarded as a primary thermochemical conversion technology which can transform woody biomass feedstocks into renewable fuels in a sustainable, economical manner [1,2]. It is flexible with respect to the types of biomass feedstocks which can be used as well as the range of renewable fuels and chemicals which can be produced [3–6]. Biomass gasification can also integrate other renewable energy sources to produce biofuels with even lower associated GHG emissions [7,8]. Biomass gasification demonstration projects targeting biofuels, e.g., bio-methane and dimethyl ether (bio-DME) have been undertaken in the EU in recent years [9–11]. In Canada, Enerkem, in partnership with City of Edmonton, recently began operating a waste-to-energy biomass gasification demonstration plant that produces bio-methanol and bio-ethanol from sorted municipal waste [12].

Biomass gasification typically occurs around 800 °C or higher, and involves thermochemical reactions of solid biomass with steam and oxygen in an oxygen-deficient environment causing pyrolysis and partial oxidation [1,2,13–16]. The process fractionates cellulose, hemicellulose and lignin constituents to yield a gaseous mixture of steam, carbon monoxide, carbon dioxide and hydrogen known as synthesis gas (or producer gas), condensable organic vapours (tar), and solid biochar. If air is used as the oxidant, the synthesis gas will also contain around 50% nitrogen, which greatly reduces its calorific value and also limits the temperature which can be achieved in the gasifier. Nitrogen can be avoided by utilizing oxygen-blown gasification or by indirect gasification, both of which can attain higher gasification temperature and improve the syngas quality [16].

Oxygenates and aromatic derivatives of benzene, which are common components of tar produced during gasification of biomass can be problematic if they condense and solidify downstream, or interfere with downstream catalytic processes. At typical reaction temperatures

during biomass gasification, tar formation is practically unavoidable and, therefore, tar removal during downstream synthesis gas cleaning is crucial in order to achieve high-quality synthesis gas at commercial scale [17–19]. This can be accomplished in part by a combination of condensation and scrubbing with a suitable solvent. Sequentially reacting the syngas over a tar-cracking catalyst at elevated temperature can greatly diminish or eliminate unwanted organics and thereby protect downstream catalyst beds from contamination [20] .

Catalytic tar cracking and steam reforming have been researched extensively, but both of these catalytic reactions continue to challenge catalyst developers to achieve lower cost, improved catalyst resistance to coking, as well as high tolerance to impurities, particularly sulphur [21,22]. Testing catalysts for tar-cracking using syngas from a biomass gasifier also poses challenges because biomass gasifiers are typically many times larger than bench-scale catalyst test units and they require kilogram quantities of catalyst. When a slip stream of syngas is used, the gasifier must be operated continuously for the duration of the testing, and this can be costly and labour intensive.

Thus, one objective of this study was to develop a bench-scale method and apparatus which could be used to cost-effectively screen catalysts for their tar-cracking ability, as well as to evaluate a catalyst's durability and sustained activity over a longer time period, prior to doing pilot-scale testing in a biomass gasifier. A second objective of the study was to evaluate how certain classes of commercial catalysts perform as gasification tar reforming catalysts. One such class of catalysts are automotive exhaust after-treatment catalysts. These three way catalysts typically utilize precious metals including rhodium, which shows high activity for tar cracking, resists coking and is more tolerant to sulphur than nickel-based catalysts [23]. They are mass produced as ceramic cordierite monolithic supports which are structurally and thermally stable. A wash coat is applied to the monolith that typically contains alumina, ceria and zirconia creating a catalyst having high surface area to support the highly dispersed platinum group metals [24,25]. Ceria promotes catalyst activity in several ways: Ce^{3+}/Ce^{4+} oxidation states in ceria impart oxygen storage capability under transient conditions; it promotes chemical activity of precious metals for water gas shift; it promotes structural stability by inhibiting particle agglomeration of the precious metals and alumina [26,27]. Modern three way catalysts are able to operate for thousands of cycles over a wide range of temperature and exhaust gas composition, under oxidative or reducing conditions. In this study we report on tests done at bench scale to evaluate tar reforming over a commercial automotive three way catalyst. Our approach aims to reduce costs to develop biomass gasification syngas cleanup by identifying commercial catalysts that perform well for tar conversion, and are readily available on the market.

2. Material and methods

A bench-scale test system for screening and evaluating catalysts for catalytic reforming of gasification tar was designed and assembled, similar to the system recently reported by Artetxe et al. [28,29]. The apparatus consisted of a stainless steel fixed bed reactor with a length of 390 mm and an internal diameter of 6 mm. The fixed bed reactor was placed in a vertical split-tube furnace capable of achieving 1000 °C. The reforming temperature for all the catalytic cracking process reactions was 700 °C. Reactor temperature set point was controlled by a K-type thermocouple in the furnace external to the reactor wall and a second K-type thermocouple embedded in the catalyst bed measured actual reaction temperature.

Tar samples were collected from CanmetENERGY's 5–20 kg/h research-scale air-blown fluidized bed gasifier, operating at a bed temperature between 800 and 820 °C. A fraction of the hot raw syngas stream, cooled to below 600 °C after exiting the gasifier, was diverted to a continuous tar fractionation system. Tar was condensed from the syngas stream stage wise in impinger vessels immersed in baths and

maintained at constant temperature. The fraction used for this study condensed between room temperature and 110 °C.

A liquid feed mixture containing methanol and water, in which 2-methoxy phenol or gasification tar was dissolved, was delivered to the reactor tube at a rate of 5 mL/h using a Harvard Apparatus precision syringe pump. A digital mass flow controller delivered a precise nitrogen flow of 50 mL min^{-1} to the catalyst bed along with the liquid feed. Notably, in order to minimize the chance of the tar compounds plugging the reactor inlet, a separate feed preheater was not used in the bench-scale setup. The liquid feed was vaporized and heated to reaction temperature in the short interval between the reactor inlet (top of the reactor tube) and the packed catalyst bed. The reforming temperature setpoint was maintained at 700 °C in all of the test runs, but the observed reaction temperature measured in the catalyst bed was typically lower.

The catalyst used in the study was obtained from a commercial automotive catalytic converter, manufactured by Walker. The catalytic ceramic monolith was removed from the converter and a portion of the monolith was broken into 1–2 mm dia. pieces. The reactor was loaded with approximately 5 g of the commercial automotive exhaust catalyst. Deactivated catalysts were subjected to a regeneration process. The catalyst was removed from the reactor and calcined in air at 500 °C for 10 h.

During a catalyst test, gaseous products exited the reactor and flowed through a chilled separator vessel where liquid products were condensed. Total product gas flow at ambient temperature was measured continuously during the catalytic cracking process using a precision wet test gas meter (Ritter TG0.5).

An on-line Agilent 6890 N gas chromatograph (GC) equipped with two thermal conductivity detectors (TCD) monitored the composition of the gaseous product stream from the catalytic testing unit at 15-min intervals throughout the duration of the catalytic cracking experiments. The composition of the collected liquid product from the separator vessel was analyzed offline using the same GC and an Agilent 5973 N mass-selective detector (MSD).

Conversion n was determined as the ratio of the sum of CO, CO$_2$ and CH$_4$ molar flowrates in the product gas to reactant molar flowrate of organic carbon in the liquid feed, and total molar flowrate of carbon coming from tar compounds was estimated using guaiacol as a representative tar compound. Equation 1 calculates conversion, which is indicative of overall catalyst reforming activity:

$$\% \text{ Conversion} = (CO + CO_2 + CH_4)product/ \sum (C)_{feed} \qquad (1)$$

Product selectivity was measured determined as:

$$\%CO \text{ Selectivity} = (CO)_{product}/(CO + CO_2 + CH_4)_{product} \qquad (2)$$

$$\%CO_2 \text{ Selectivity} = (CO_2)_{product}/(CO + CO_2 + CH_4)_{product} \qquad (3)$$

$$\%CH_4 \text{ Selectivity} = (CH_4)_{product}/(CO + CO_2 + CH_4)_{product} \qquad (4)$$

The pre-, post-use and the regenerated catalyst were imaged with a Hitachi S–3400 N scanning electron microscope (SEM) equipped with an Oxford Instrument X-Max 20 mm^2 silicon drift detector controlled with AZtec version 3.4 software. The accelerating voltage was 20 kV and the working distance was approximately 10 mm.

3. Results and discussion

3.1. Characterization of gasification tar

Dense gasification tar which was condensed and collected in our pilot-scale gasifier, was analyzed by gas chromatography with a mass selective detector (GC–MS). Fig. 1 shows the total ion chromatogram (TIC) for a volatile dense gasification tar. The GC–MS identified 33 compounds using the built-in NIST mass spectral library, and about half of those, whose ion signal contributed 1% or more to the total area of