ABSTRACT

This paper deals with the characterisation of tar from two configurations of bioresidue thermochemical conversion reactors designed for producer gas based power generation systems. The pulverised fuel reactor is a cyclone system (R1) and the solid bioresidue reactor (denoted R2) is an open top twin air entry system both at 75-90 kg/h capacity (to generate electricity $\sim 100$ kVA). The reactor, R2, has undergone rigorous test in a major Indo-Swiss programme for the tar quantity at various conditions. The former is a recent technology development. Tars collected from these systems by a standard tar collection apparatus at the laboratory at Indian Institute of Science have been analysed at the Royal Institute of Technology (KTH), Sweden. The results of these analyses show that these thermochemical conversion reactors behave differently from the earlier reactors reported in literature in so far as tar generation is concerned. The extent of tar in hot gas is about 700-800 ppm for R1 and 70-100 ppm for R2. The amounts of the major compounds — naphthalene and phenol — are much lower that what is generally understood to happen in the gasifiers in Europe. It is suggested that the longer residence times at high temperatures allowed for in these reactors is responsible for this behavior. It is concluded the new generation reactor concepts extensively tried out at lower power levels hold promise for high power atmospheric gasification systems for woody as well as pulverisable bioresidues.

INTRODUCTION

Thermochemical conversion of biomass to combustible gas has received growing interest in developing countries due to economic compulsions and in developed countries due to environmental considerations. The conversion process, also termed
Gasification, produces gaseous fuel which can be used in reciprocating internal combustion engines or gas turbines. The conversion process is accompanied by generation of tar and particulates the concentration of which in the gas is to be limited in order to enable smooth engine operation. Many tar components can get deposited in the transfer lines and engine valves and after a few hundred hours of operation, serious “hard” cleaning procedures may need to be initiated. The nature and magnitude of tar is dependent on the design of the reactor, in particular the thermal and oxidative environment that the mixture subjected to in the reactor. An analysis of tars is considered useful as it may provide clues to the operational features of the reactor and to indicate possible improvements in design of the reactor.

Simell and Brendenberg [1] have reported composition of tar after catalytic cracking from a high power updraft gasifier. The results reported in their paper indicate that the amount of benzene is very large. Benzene may not be a “bad” tar component, since it can be carried into the engine without the problem of deposition. Amongst benzene derivatives, toluene is large while phenol and naphthalene constitute the next largest fractions. The sum of the other complex compounds is by no means small even after a tar purifying system. The compounds like naphthalene are likely to deposit in the ductings and valves.

Paztor and Kristoferson [2] have presented a summary of the composition of tar from a range of gasifiers (Table 1, col.2-4). This table confirms the generally known set of facts that downdraft wood gasifier produces much less tar compared to updraft wood gasifier and throatless rice husk gasifier. Both updraft and rice husk gasifiers, more particularly the latter, seem not to have much of a tar cracking process inside the reactor. The composition of the tar is such that the lower end compounds like phenols and cresols are in more copious measure compared to higher and more complex ones, again indicating to poor tar cracking in the reactor.

Tar can be thought of as being composed of several compounds of different nature such as acidic, neutral and basic components. The acidic components are acids and phenols and the neutral compounds are generally polyaromatic hydrocarbons (PAH) while all nitrogen containing compounds (N-organics) form the basic component.

EXPERIMENTAL

Gasifiers and tar sampling

The cyclone reactor for pulverised fuels (R1)

The cyclone reactor [3] consists of a tangential port for heating the reactor as a part of the start-up system and also for introducing the pulverised fuel along with air. The schematic of the reactor is shown in Fig. 1. The reactor has ceramic lined mild
<table>
<thead>
<tr>
<th>Tar component</th>
<th>Updraft†</th>
<th>downdraft†</th>
<th>R2†</th>
<th>Gasifier R1†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Throatless</td>
<td>With throat</td>
<td>Hot end</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Rice husk)</td>
<td>(Wood)</td>
<td></td>
</tr>
<tr>
<td><strong>Mixed oxygenates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td>600-1800</td>
<td>4600</td>
<td>20-100</td>
<td>11.04</td>
</tr>
<tr>
<td>Cresols</td>
<td>1200</td>
<td>2400</td>
<td>10</td>
<td>1.27</td>
</tr>
<tr>
<td>Dimethyl phenol</td>
<td>-</td>
<td>2500</td>
<td>-</td>
<td>2.45</td>
</tr>
<tr>
<td><strong>Polyaromatic hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>-</td>
<td>400</td>
<td>50-140</td>
<td>16.20</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>-</td>
<td>14</td>
<td>10-70</td>
<td>2.25</td>
</tr>
<tr>
<td>Anthracene</td>
<td>-</td>
<td>2</td>
<td>10-70</td>
<td>1.16</td>
</tr>
<tr>
<td>Pyrene</td>
<td>-</td>
<td>2</td>
<td>10-70</td>
<td>5.82</td>
</tr>
<tr>
<td>Fluorene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.71</td>
</tr>
<tr>
<td>Methyl naphthalene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.82</td>
</tr>
<tr>
<td>Indene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.62</td>
</tr>
<tr>
<td>Xylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.63</td>
</tr>
<tr>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>34.62</td>
</tr>
<tr>
<td>Unknown§</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>107.70</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>211.43</td>
</tr>
</tbody>
</table>

† From Reference 2. † Present study
§ Poly aromatic hydrocarbons which have not been identified. All basic compounds are included in this.

Steel shell, of 0.5 m inner diameter and height 1.8 m including the conical region. Normally the bottom of the reactor is open to the ambient through a small exit duct to enable removal of the residue. A screw feeder and a blower are used to convey the pulverised fuel (in this case, rice husk pulverised to less than 1 mm) and air using the tangential entry into the cyclone reactor. The reactor system is started by heating the reactor wall using a kerosene burner to 600°C. Then a small amount of powdered biomass is fed to the reactor for the temperature to build up. The reactor is switched over to gasification mode, after this stabilization, by increasing the fuel feed. Figure 1 also shows the tar sampling points.
The downdraft woody biomass reactor (R2)

The gasifier shown in Fig. 2 consists of a cylindrical ceramic lined reactor with air entering through the open top and a set of air nozzles about 250 mm above the grate [4]. The reactor has an annular of a stainless steel section of about 1 m length at the top, through which hot gas is passed through. The hot gas which enters the annulus around 500°C, transfers about 4 to 8% of the heat to the wood chips inside, improving the thermal efficiency of the system, in addition to drying the wood chips in this zone. The inner wall temperature reaches more than 350°C after a few hours.
Figure 3: Tar sampling train for pulverised fuel gasifier

of operation at full power and this helps in drying and preheating of wood chips. In this system air flow through the fuel bed is nearly one-dimensional, and moves to a final fuel rich condition from an initial lean state through stoichiometry.

Tar Sampling apparatus and method

Gas samples are drawn isokinetically from the main gas line at locations identified in Fig. 1 and 2. The sampling train in the powdery biomass gasifier (R1) shown in Fig. 3 consists of four empty traps, one wash bottle with water, one wash bottle with methylene chloride, and one more empty trap, all in series, kept at low temperature (close to $0^\circ$C using freezing mixture). The gas sample is drawn through the sampling apparatus and a gas meter using a vacuum pump. The outlet of the vacuum pump is connected to a burner to burn the gas. This facility is also used to check if any air leakage into the sampling train by the inspection of the flame in the burner. A diffusion flame is taken to indicate no leakage while a premixed flame will indicate leakage. Amount of gas drawn through this train is directly read from the integrated gas flow meter. Tar sample is collected from about 1.8 to $2 \text{ m}^3$ of gas in each experiment (at a rate of $1 \text{ m}^3/h$). At the end of the experiment, all the gas line between the valve below the sampling probe and the gas flow line is washed with methylene chloride for any tar/dust sticking in the line and is added to the tar/dust collected in the cold traps. Tar thus collected is dissolved in methylene chloride and filtered to separate any dust collected along with tar. About 100 to 150 ml of water is collected in the traps along with tar. This water is separated from tar dissolved in methylene chloride using a separating funnel. Trace amount of water in the organic phase is removed with anhydrous sodium sulfate. Tar thus collected is weighed after slow evaporation of methylene chloride at room temperature.
For the tests on downdraft woody biomass gasifier, R2, the procedure identified by Swiss scientists was used both at Bangalore, India and Chatel-St-Denis, Switzerland [5]. The schematic figure is shown in Fig. 4. The apparatus is designed to run for 6–10 hours. It consists of a series of wash bottles—two of 3 l and five of 2 l capacity. The gas was bubbled first through the 3 l bottle filled to one-third (1000 ml) capacity with water to remove dust and moisture and taken to another empty bottle to trap any droplets which are carried over. These two bottles are kept in freezing mixture. The gas from the empty bottle is allowed to bubble through a series of three bottles, one-third filled with anisole (650 ml; used as solvent for dissolving tar), and through an empty bottle to collect any carried over anisole droplets. At the exit of the empty bottle, thimble filters amounting to an area of 500 cm² are provided in another 3 l bottle, to trap any particulates escaping the sampling bottles. The gas after being pumped out of the system by a vacuum pump pass through a gas meter for monitoring the flow rate and a flow integrator to obtain the total gas sampled before going to a swirl burner. Extensive procedures (both pressure and vacuum test) are carried out to ensure that the sampling system is leak proof. At the end of the sampling, all the tar in water and empty traps is extracted with anisole and added to the anisole phase. Any water in the anisole phase is dried using anhydrous sodium sulfate and the anisole phase is made up to a known volume before drawing aliquots for analysis.

The main difference between the above two methods of tar sampling is that the amount of tar collected can be independently verified in the former case by weighing where as in the latter method only GC route is used to establish the amount of tar.
produced since it is not possible to evaporate the solvent at low temperature. The amount of tar collected in the first method is estimated using quantitative GC traces as well as by physical weighing. Results from these two methods are in good agreement in the present work.

Char bed cleaning

It was hypothesized that char which has reactive carbon as well as some inorganic matter could be a tar reduction agent. In the case of pulverised fuel gasifier (R1), in order to determine the possibilities of the rice husk char from the gasifier acting as tar cracking medium, a fluidized bed was made by directly drawing the hot char from the gasifier. The fluidising column or fluidiser (Fig. 1) is a vertical column of 600 mm diameter made of SS 304 with an opening for the hot gas, an opening for hot char and ash mixture, a gas distributor or grid plate and a bin for residual char collection.

The hot gas enters below the grid plate, which and consists of arrays of holes of 2 mm diameter and 2 mm pitch. The plate is integrated in four halves wherein each portion has holes directed so as to give an overall swirl effect. The char from the reactor exit is conveyed to fluidiser through a 35 mm diameter tube connected at 45 mm above the grid plate. The exit of the gas along with carry over of char and ash is connected to a cyclone. The residence time for gas with hot char in the column is around one second and temperature of the bed is in excess of 500°C. Tar sampling experiments were carried out before and after the fluidized bed.

Operation of the gasifiers for tar collection

The gasifiers are operated for a period of 1-3 hours before steady operating conditions are reached. The cyclone gasifier (R1) was operated with pulverised rice husk. The fuel feed rates are 80 kg/h and measured air-to-fuel ratio is 0.97. The wall temperatures reach steady values between 750 and 850°C in an hour and a half. Tar sampling is performed for two hours after steady conditions are reached.

The wood gasifier (R2) is run on causarina at a wood consumption rate of 18 kg/h by slowly raising the feed rate and maintaining the constant feed rate such that some of the wall temperatures cross 450°C and the operation of the reactor stabilises at this level. The measured air-to-fuel ratio is 1.7. The gas is drawn through the isokinetic sampling system at 2 m³/h for 5 h into the tar collection system. The total amount of gas sampled in the case of wood gasifier is much more than for cyclone gasifier since the expected amount of tar for wood gasifier is very small.
Chemical Separation methods

The separation and analysis are similar to the procedures reported earlier [7, 8]. A known amount of tar is dissolved in about 25 ml of dichloromethane. The basic components, N-organics, are extracted with two 10 ml aliquots of 0.1M H₂SO₄. The dichloromethane layer with neutral and phenolic compounds is washed with 10 ml of water and the washings are added to the acidic layer. The dichloromethane layer is made up to 25 ml using a standard measuring flask after drying over anhydrous sodium sulfate. SPE (Solid Phase Extraction) on aminopropylsilane phase is used to separate neutral and phenolic compounds of tar.

The column is conditioned with 400 µl of dichloromethane. 100 µl of the organic phase mixed with known quantities of internal standards, t-butylcyclohexane and p-ethoxyphenol, are added to the column and eluted with 400 µL (100 µL aliquots) of dichloromethane. This process separates all the neutral aromatic compounds from the phenolic compounds which are adsorbed in the column. The phenolic compounds are eluted by 200 µL of a mixture of 2-propanol and dichloromethane (1:1 v/v) and by 300 µL of 2-propanol. About 50 µL of BSTFA is added to the phenolic fraction for derivatization. The derivatization is used to improve the GC column performance of the phenolic compounds.

The N-organics are extracted using reverse-phase (n-C₁₈) SPE. The SPE cartridge is preconditioned in turn with acetonitrile, water and a phosphate buffer (pH=10.8). After pH adjustment to ~ 12 (0.1M NaOH), a known quantity of the internal standard, 2,4,6-trimethyl pyridine, in EtOH is added to the sample and this mixture is passed through the SPE under reduced pressure. The retained N-organics are eluted with a mixture of dichloromethane, acetonitrile and diethylamine (1:1:0.1 v/v) at a flow rate of 1-2 drops/s.

GC Analysis

GC analyses are carried out on a gas chromatograph equipped with a split injector (280°C) and flame ionization detector (300°C) using helium (head pressure 120 kPa) as carrier gas. Samples are separated on a 25 m x 0.25 mm i.d. fused silica capillary column coated with 0.4 mm chemically bonded cross-linked silicon (95 % dimethyl + 5 % phenyl) CP-Sil 8 CB phase. N-organics are analyzed using a temperature programme running from 90°C to 180°C at 5°C/min with an isothermal period of 3 min at 90°C. Phenols and aromatics are analyzed using a temperature program running from 90 to 300°C at 8°C/min with an isothermal period of 3 min at 90°C.

Peaks are automatically calculated by an integrator. Quantification was performed.
Table 2

Amount of tar collected per cubic meter of gas in cyclone as well as down draft gasifiers.

<table>
<thead>
<tr>
<th>Description</th>
<th>Cyclone Gasifier</th>
<th>Downdraft</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Char bed</td>
<td>After Char bed</td>
</tr>
<tr>
<td>Tar mg/m³</td>
<td>748.4</td>
<td>438.0</td>
</tr>
</tbody>
</table>

Table 3

Neutral, Acidic and Basic fractions of tar from cyclone gasifier.

<table>
<thead>
<tr>
<th>Tar component</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Char bed</td>
</tr>
<tr>
<td>Neutral</td>
<td>98.66</td>
</tr>
<tr>
<td>Acidic</td>
<td>1.14</td>
</tr>
<tr>
<td>Basic</td>
<td>0.20</td>
</tr>
</tbody>
</table>

on the basis of response factor for analytes, relative to the internal standards using at least three-point calibration curve. Identification was based on analyte retention times relative to those of the internal standards and by comparison with GC patterns obtained for similar samples.

RESULTS AND DISCUSSION

The amount of tar collected per cubic meter of the gas in the two gasifiers are given in Table 2. As can be seen, the hot tar generated in woody biomass gasifier (R2) is about a tenth of that in cyclone gasifier (R1). The value in cyclone gasifier (R1) is also small compared to the fluidised bed systems meant for agro-residues [6]. The three fractions (acidic, neutral and basic) are shown in Table 3. It can be seen that 98.6% of the fraction collected is neutral and the remaining 1.4% is shared between acidic and basic components. As one would expect, the composition of tar is different from pyrolitic oils which are highly acidic in nature. Figures 5, 6 and 7 show the results of GC analysis of the three fractions of tar from R1. Figure 5 shows the GC of the neutral fraction. A simple inference from the figure would be that naphthalene content of the tar is very low compared to several higher fractions. Small molecules such as Toluene, indene seem to be missing in the neutral fraction where as the amount of higher fused ring compounds such as antheracene, etc. are the major compounds. There is concern if the regions marked “A” on Figure 5 and 7 are real or artifacts caused by plasticizer or other such components dissolved in the solvent during handling/sampling. If these are eliminated, the actual amount of
Figure 5: GC trace for neutral fraction for pulverised fuel system

Figure 6: GC trace for phenolic fraction for pulverised fuel system

Figure 7: GC trace for phenolic fraction for pulverised fuel system
tar fraction will be much lower than that is indicated by the analysis. Further work is in progress to clarify this matter.

Figure 6 shows GC of phenolic fraction of tar and this trace appears bereft of any such artifacts. From the figure it is clear that the total amount of phenolic compounds generated is very low compared to the neutral compounds. In low temperature gasification, in general, it is expected that gasifiers produce nearly equal amounts of phenolic and neutral compounds. It may be noted from the figure that in the present case the phenolic fraction amounts to only 1.15% of the neutral fraction.

The GC of N-organics, basic fraction of tar, is given in Figure 7. The basic compounds in the tar produced is as low as 0.2%. The compounds identified in this fraction are almost exclusively pyridine and minor amounts of substituted pyridenes and quinolines.

The results for wood gasifier (R2) shown in Figures 8 and 9 generally confirm the qualitative behaviour described above. A closer look at the GC traces of neutral compounds reveals that the amount of higher fused rings is negligible compared to that from cyclone gasifier, a feature providing better acceptance from the point of view of GC analysis; the absence of artifacts of the kind found in Figure 5 and 7 is helpful. If the portion marked "A" in Figure 5 and 7 are considered real, then the main reason for the difference between R1 and R2 is possibly the long residence time of the tar in the high temperature reduction zone (~ 2 s) in the case of the downdraft wood gasifier (R2).
All the results including the magnitudes of various components are put together with results from literature in Table 1. Several observations are made on this Table. The results for cyclone gasifier (R1) show a much lower tar content even at hot conditions in comparison to throatless open top systems used for rice husk. This is a result of three features. Firstly, the rice husk used in the present reactor is pulverised with varying sizes. This allows for uniform heat release inside the reactor and better thermal environment. Secondly, the mean gas residence time inside the reactor is about 1.8 to 2 s. The third feature is that measurements have shown that char conversion inside the reactor is about 50 % (rice husk has 60 % volatiles, 20 % char and 20 % ash. Of the 20 % char, 50 % is converted inside the reactor). Because of the more benign thermal and chemical environment, it is inferred that the tar content is low compared the classical open top system. The results of cyclone system after the char bed show that the differences in some cases are small, but in a few cases like phenanthrene and acenaphthylene char bed reduces the amount substantially. However, the amount of unknown compounds (those which could not be identified) has increased.

The role of the char bed in tar conversion is seen from the last column of Table 1. There seems to be a reduction of the total amount of tar from about 1358 mg/kg dry biomass to 818 mg/kg dry biomass. Also the composition of tar is different in the two cases. Both phenanthrene and Acenaphthylene are significantly reduced. Some of the reactions have led to an enhancement of the “unknown category” indicating to the formation of more complex structure due to thermal/catalytic effects. While more data of this kind need to be generated before firm conclusions can be drawn; these results by themselves are very interesting.

In the case of woody biomass system (R2), the values of various tar components are generally smaller than for cyclone system. In this case also an assessment of the gas residence time through the reactor is about 2 s of which the first portion of 1 s is completed by the time the gas reaches the air nozzles and another second below the air nozzles for combustion/reduction reactions. Because of the more homogeneous supply of the gases through a double traversing of the hot zone, the cracking of the compounds and their conversion to some lower sized species takes place. This is evident from the GC trace of the neutral component (Fig. 8) that there is not much of fused ring compounds.

Amongst the various designs, the updraft gasifier for wood residues and throatless open top systems for rice husk occupy high positions as “tar generators”. While in the former case, the arrangement almost invites lower molecular weight liquid components to be evolved out of the reactor without virtually any cracking, in the latter case, the fact that rice husk is not pulverised and the thermal environment is not entirely benign leads to high tar generation.
CONCLUDING REMARKS

Pulverised biomass cyclone gasifier (R1) when used with rice husk produced about 750 ppm of tar. The analysis tar has showed the presence of very low naphthalene content in the neutral fraction. Phenolic fraction present in the tar was not more than 1.2%. The reasons for the low phenolic and naphthalene content are surmised as being due to adequate residence time in zone where reactive char is present with the right thermal environment. The inclusion of the char bed appears to have led to cracking of the tar and its consequent reduction by 40%

In the case of wood gasifier (R2), the reactive wood char with low ash content and the more homogeneous gaseous environment and adequate residence time all seem to have helped in reducing the tar to very low levels (77 ppm) in comparison to cyclone gasifier.

Both the reactors seem to produce very low levels of naphthalene and phenols. This should be sufficient incentive to base designs of gasifiers along present ideas for much higher power levels than currently realised.

ACKNOWLEDGEMENT

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REFERENCES


