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TAR REMOVAL IN A FIXED BED WITH APPLICATION TO BIOMASS GASIFICATION

Z. Abu El-Rub[*a], E. A. Bramer[a], G. Brem[a,b]

[a]University of Twente, Laboratory of Thermal Engineering, P. O. Box 217, 7500 AE Enschede, The Netherlands
[*]Fax: +31534893663, Tel: +31534891091, Email: z.y.abuelrub@ctw.utwente.nl
Fax: +3153 4893663, Tel: +31534892530, Email: e.a.bramer@ctw.utwente.nl
[b]TNO, P. O. Box 342, 7300 AH Apeldoorn, The Netherlands
Fax: +31555493287, Tel: +31555493290, E-mail: g.brem@mep.tno.nl

ABSTRACT: A project is carried out to develop a new approach for tar elimination process downstream of a gasifier making use of cheap and active materials as catalysts. These catalysts convert tar in the producer gas to useful gases. In the first stage of the project screening of catalysts was carried out in a fixed bed tubular reactor. The results of the fixed bed experiments will be used in the design of the process. This paper presents a preliminary testing of the selected catalysts. The selected catalysts are dolomite, olivine, spent FCC catalyst, and char. The efficiency of tar removal for these materials was compared with that of an inert material (sand) and with that of high activity material (commercial nickel catalyst). In addition, the thermal stability of the tar was tested in the temperature range of 700 to 900 ºC. Tar decomposition over the different catalysts was modeled by reaction with CO_2 and steam. In a previous work, tar decomposition over these materials was studied using naphthalene as a tar model compound which is a light polyaromatic tar. In this paper, results were discussed for a study on tar decomposition using phenol which is a heterocyclic aromatic with a concentration of 8-12 g/Nm^3. The testing was carried out in a fixed bed at temperatures of 700 and 900 ºC under atmospheric pressure and a gas residence time in the catalyst bed with respect to empty reactor of 0.3s. The gas composition and tar content in the gas were analyzed downstream the reactor using on-line and off-line gas analysis. The on-line gas analysis was done by a GC with flame ionization (FID) and thermal conductivity (TCD) detectors. In The off-line gas analysis, the gas was sampled using solid-phase adsorption (SPA) sampling method and analyzed with gas chromatography and mass spectrometry (GC/MS).
Keywords: tar elimination; phenol; catalysts

1 INTRODUCTION

The contribution of biomass to the world's energy supply is presently estimated to be around 10 to 14 % [1]. Biomass can be defined as any organic material of plant origin. It is expected that biomass gasification technologies will be an important part of the attempt to meet the goals of expanding the use of biomass. Gasification involves partial combustion of biomass to produce gaseous fuels (fuel gases or synthesis gases) by heating in a gasification medium such as air, oxygen or steam. These gaseous products have many applications such as[2] heat or electricity generation, synthesis of liquid transportation fuels, hydrogen fuel production, synthesis of chemicals, and fuel cells. In general, tar can be removed by physical tar elimination processes, non-catalytic tar elimination (e.g., thermal cracking), and catalytic tar elimination. Catalytic tar conversion is technically and economically interesting approach for gas cleaning. Such approach is intuitively interesting because it has the potential to increase conversion efficiencies while simultaneously eliminating the need for collection and disposal of tar. However, the catalytic conversion of tar is commonly known as hot gas cleaning.

Model tar compounds are simple molecules chosen as substitutes for real tar mixture. Since tar is a complex mixture of hydrocarbons, it is difficult to prepare and to study its conversion. To simplify studying tar conversion, tar components are segregated and classified into five classes based on their chemical, condensation and solubility behavior, as shown in Table 1 [3].

The tar classification system has been developed by ECN, TNO and UT in the project "Primary measures for the reduction of tar production in fluidized-bed gasifiers", funded by the Dutch Agency for Research in Sustainable Energy (SDE). An extensive description of the tar classes is given in the first progress report "Tars in Biomass Thermochemical Conversion Processes" by N. Padban [4].

Table 1. Classification of tar [3]

Class	Tar components
1	GC undetectable tar. (heaviest tar)
2	Heterocyclic components (like phenol, pyridine, and cresol). These are components that generally exhibit a high-water solubility
3	Aromatic components. Light hydrocarbons which are important from the point view of tar reaction pathways, but not in particular towards condensation and solubility (e.g., toluene and xylene, not benzene)
4	Light polyaromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures.
5	Heavy polyaromatic hydrocarbons (4-5 rings PAH's). These components condense at relatively high temperature

The catalytic activity of several selected catalysts was tested for tar elimination. The selected catalysts are dolomite, olivine, spent FCC catalyst, and biomass char. The efficiency of tar removal for these materials is compared with that of an inert material (sand) and with that of high activity material (commercial nickel catalyst). Tar decomposition over the different catalysts was modeled by reaction with CO_2 and steam. In previous works [5,6], class 4 of tar modeled by naphthalene was tested. In this paper, class 2 of tar modeled by phenol is tested.

2 EXPERIMENTAL

2.1 Apparatus

The experiments were performed in a tubular reactor at atmospheric pressure and a temperature of 700-900 ºC. The feed gas is typically 70 $L.h^{-1}$ (STP). The gas (N_2) is metered from a cylinder controlled by critical nozzles. The nitrogen is used as the carrier gas, which flows through phenol and water saturation units made from glass. The desired mole fractions are obtained by controlling the temperatures of the saturation units. CO_2 is added to the feed gas and the mixture is passed through the reactor. The reactor is an empty quartz tube with an internal diameter of 4 cm and a length of 90 cm, and

heated by a tubular electric furnace. The reactor has two thermocouples, the first is in the center (considered as the reference temperature) and the second is close to the wall. These two thermocouples can be moved along the bed height in small quartz pipes to measure longitudinal temperature profiles. Temperatures are measured by K-type thermocouples. The bed material is supported by a porous quartz disc, which allows the gas to pass through its bottom. The catalyst is placed above a bed of an inert silica sand of equal height to the catalyst bed. Fig. 1 shows the scheme of the setup.
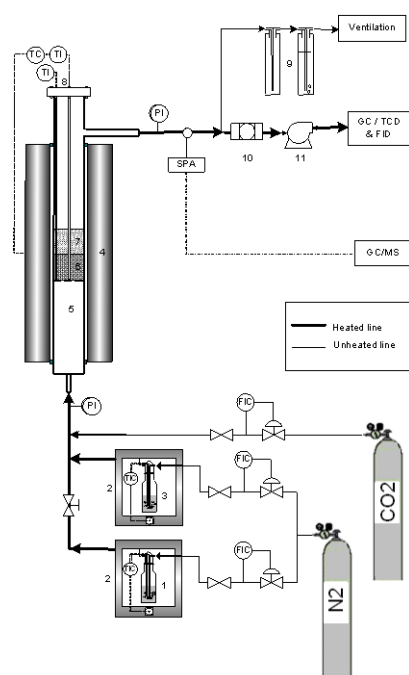

Figure 1. Experimental setup
1. water saturator; 2. oven; 3. phenol saturator; 4. tubular furnace; 5. quartz tubular reactor; 6. inert bed; 7. catalyst bed; 8. quartz tubes for thermocouples; 9. water condenser; 10. filter; 11. heated pump; GC: gas chromatography; FID: flame ionization detector; TCD: thermal conductivity detector; MS: mass spectrometry; SPA: solid phase adsorption

2.2 Test procedure

The experimental runs were started by pouring a weighed sample of the bed material (catalyst) on the reactor grid. The feed gases flow rates were regulated to give the desired space time, which is 0.3s. The feed gas composition is 5 vol.% CO_2, 10 vol.% H_2O, 8-12 g/Nm^3 tar and the balance is N_2. Dolomite calcination was carried out in situ at the treatment temperature and atmospheric pressure for 1 h at constant nitrogen flow. After calcination, all the gaseous reagents were fed and the reactor is heated to the required temperature. The catalysts were then stabilized for at least 15 minutes before tests were started.

2.3 Tar analysis

The gas composition and tar content in the gas are analyzed downstream the reactor using on-line and off-line gas analysis. The on-line gas analysis is done by a GC with flame ionization (FID) and thermal conductivity (TCD) detectors. In The off-line gas analysis, the gas is sampled using solid-phase adsorption (SPA) sampling

method and analyzed with gas chromatography and mass spectrometry (GC/MS).

2.4 Catalysts

Dolomite, olivine, nickel and "in-equilibrium" (once used) fluid catalytic cracking (FCC) catalyst were obtained from commercial suppliers. Char was produced from wood biomass in our laboratory. Char is produced by pyrolysing the biomass wood at 700 ºC. FCC catalyst was obtained at an average particle size of 57 μm. The particles of dolomite, olivine and char were sieved to a particle size range of 1.40-1.70 mm. Nickel catalyst particles were crushed and sieved to particle size range of 1.4-1.7 mm. Table 2-4 show some chemical characteristics of the catalysts.

Table 2. Chemical composition of the catalysts (wt.%)

Element	Olivine	Dolomite	Nickel
MgO	48.5-50.0	21.5	-
CaO	0.05-0.10	30.5	-
SiO_2	41.5-42.5	0.15	7
Fe_2O_3	6.8-7.3	0.20	-
Al_2O_3	0.4-0.5	0.061	12
NiO	0.3-0.35	-	70
MnO	0.05-0.10	-	-
Cr_2O_3	0.2-0.3	-	-
$NiCO_3$	-	-	5
K_2O	-	-	-
BET Surface area (m^2/g)	<1	9.67	n.a
Average pore diameter ºA	-	182.2	n.a
Apparent density, kg/l	6.58	6.45	3.43

n.a = not analyzed

Table 3. Chemical characteristics of FCC catalyst

APS μ	SA m²/g	MSA m²/g	ABD g/cc	Fe wt.%	Na wt.%
57	172	79	0.86	0.3	0.15
C wt.%	Ti wt.%	ReO wt.%	SiO2 wt.%	Mg wt.%	Al_2O_3 wt.%
0.08	0.97	3.73	50.58	0.21	44.3

Table 4. Ultimate biomass char analysis (wt. %)

Element	Dry	daf
C	92	93
H	2.45	2.5
O	3	3
N	0.53	0.54
S	1	1.01

3 EXPERIMENTAL DATA EVALUATION

3.1 Tar conversion

The conversion of the tar model compound (phenol) was calculated from the inlet and outlet phenol concentrations of the gas. This tar elimination includes catalytic conversion as well as thermal cracking. Tar conversion reactions are related to steam and dry (CO_2) reforming reactions with the model tar component. The tar conversion is defined as:

$$X = \frac{(C_{in} - C_{out})}{C_{in}}$$
(1)

3.2 Residence time

The residence time (τ) in the catalyst bed with respect to the empty reactor is defined as:

$$\tau = \frac{V_{R,cat}}{Q(T, P_{tot})}$$
(2)

4 RESULTS AND DISCUSSION

Two types of experiments were performed, thermal (without a catalyst) and catalytic tar elimination. The thermal experiments were performed to study the stability of phenol in the temperature range of 700 to 900 °C. Six different bed materials were used to study their catalytic effect on phenol (tar) conversion. For both types of experiments, dry gas and tar analysis ware performed. The summary of these experiments is shown in Table 5.

The thermal experiments have shown the following results:

- Increasing the treatment temperature caused an increase in both H_2 and CO concentrations and a decrease in CO_2 concentration. This can be explained by increasing the rates of steam and dry reforming reactions as the temperature increases.
- Phenol is stable at a temperature of 700 °C with only 6.3 wt.% conversion. However, it lost its stability as temperature increased with more than 97wt.% conversion at 800 °C and more than 98 wt.% at 900 °C.
- No significant amounts of other tars were formed.

The catalytic experiments were performed at two temperatures: 700 and 900 °C. The following results were obtained:

At 900 °C:

- All bed materials gave 100 wt.% tar conversion. More than 98 wt.% of phenol is thermally eliminated, and the bed materials eliminated the remaining 2 wt.% tar.

At 700 °C:

- Unexpectedly, silica sand showed significant catalytic activity for phenol conversion, about 34 wt.%.
- Dolomite and nickel gave almost complete tar conversion (99.9 wt.%). Both gave high H_2 and CO concentrations. This confirms that dolomite is like nickel a reforming catalyst.
- Char produced the highest concentrations of H_2 and CO and moderate tar conversion (82 wt.%). This is mainly because of the gasification reactions that occur to the char which caused a loss of char.
- Olivine gave poor tar conversion (43wt.%). The dry gas analysis showed that it is also not a reforming catalyst, but could be a cracking catalyst.
- FCC gave a moderate tar conversion (87 wt.%). The dry gas analysis showed that it is not a reforming catalyst, but as known a cracking catalyst.
- No significant amounts of other tars were formed.
- The comparison of activity of these catalysts is shown in Fig. 2.
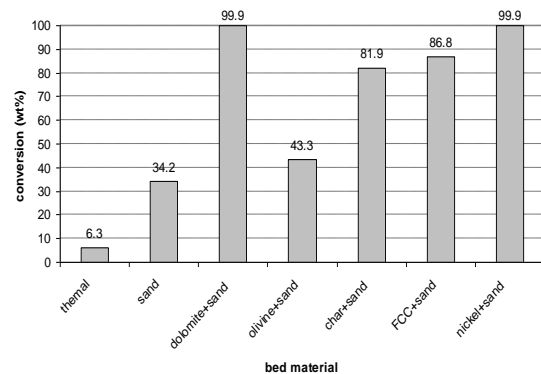

Figure 2. Effect of bed materials on conversion of the model tar component (phenol). Bed temperature 700 °C, initial tar concentration 8-12 g/Nm³, reactor pressure 1 atm and gas residence time 0.3 s.

Table 5. Dry gas and tar composition at the fixed bed reactor outlet for thermal and catalytic tar conversion. Catalytic treatment temperatures 700 and 900 °C, residence time 0.3 s, feed gas composition (5 vol.% CO_2, 10 vol.% H_2O and 85 vol.% N_2), and inlet tar concentration 8-12 g/Nm³.

T (°C) Component (vol.%)	Thermal*			Silica sand		Dolomite		Olivine		Char		FCC		Nickel	
	700	800	900	700	900	700	900	700	900	700	900	700	900	700	900
H_2	0.14	1.16	1.60	0.23	1.0	0.85	0.40	0.27	1.0	2.18	5.09	0.19	0.89	1.93	0.08
N_2	93.83	93.14	92.58	93.40	93.0	93.33	93.07	93.67	95.0	89.08	82.56	94.08	93.37	90.0	93.45
CO	9.8e-4	2.6e-3	2.5e-3	9.1e-4	2.6e-3	2.6e-3	2.6e-3	7.4e-4	2.5e-3	1.5	9.2	9.3e-4	2.6e-3	1.9	1.2e-3
CO_2	6.03	5.70	5.82	6.37	6.0	5.83	6.52	6.07	4.0	7.23	3.19	5.73	5.74	6.22	6.47
Tar-out (mg/Nm³)	1091	25	21	784	0	1	0	627	0	158	0	112	0	1	0
Tar-in (mg/Nm³)	1164	1142	1238	1192	908	995	1351	1105	1090	871	789	847	982	1114	1005
Conversion (wt.%)	6.3	97.8	98.3	34.2	100	99.9	100	43.3	100	81.9	100	86.8	100	99.9	100

* empty reactor

5 CONCLUSIONS

- Phenol is stable at a temperature of 700 ºC. However, it is not stable at 800 ºC or above.
- Thermal cracking of phenol is important and more than 98 wt.% conversion is obtained at 900 ºC.
- Phenol is converted mainly because of reforming and thermal cracking reactions.
- All bed materials gave complete phenol conversion at 900 ºC.
- Dolomite and nickel have almost 100 wt.% phenol conversion and their catalytic behavior is similar.
- Olivine showed a poor catalytic activity and sand was not inert as thought to be.
- Char catalyst is lost due to gasification reactions with steam and CO_2.
- The order of activity of these catalysts was found to be: commercial nickel = dolomite > FCC > char >> olivine > sand.

ACKNOWLEDGEMENT

NOMENCLATURE

C_{in}	Inlet tar (phenol) concentration to the reactor, $g.m^{-3}$
C_{out}	outlet tar (phenol) concentration to the reactor, $g.m^{-3}$
P_{tot}	Total pressure, Pa
Q	Volume flow rate, $m^3.s^{-1}$
T	Reaction temperature, ºK
$V_{R,cat}$	Volume of catalyst bed with respect to the volume of empty reactor, m^3
X	Conversion of tar (phenol), $g.g^{-1}$
τ	Residence time with respect to the empty reactor, s

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