

INVESTIGATION OF TAR PROPERTIES FOR TAR REMOVAL BY SCRUBBING

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ABSTRACT: A new concept to remove tar by scrubbing from biomass gasification gas is investigated. The concept is based on a system capable to remove the tars in two sequential stages: heavy tars are removed in a first hot absorber and the light tars (and water) are removed in a second, colder, absorber. The liquid stream contain light tars is recirculated to the first absorber to be used as primary solvent. Key data (viscosity and the melting temperature of various liquid mixtures) are investigated to preliminary assess the performance of the proposed system.

Keywords: tar, biomass, gasification, absorption, dew-point.

1 INTRODUCTION

Gasification is an interesting route for conversion of wastes and biomass materials to useful gaseous products: fuel gas for direct firing in thermal applications, such as kilns and boilers, co-firing in existing coal-fired boilers, gas for engines, turbines and fuel cells generating electricity, as well as raw gas for production of fuels or chemicals. The presence of tars in the biomass product gas is still one of the biggest problems to be solved for applications different for direct use of the gas in thermal applications. Tar is formed in the gasifier and comprises a wide spectrum of organic compounds, generally consisting of several aromatic rings [1-2].

Removal of tars by condensation is, in principle, the easiest way to remove tars. Various cooling methods have been applied in biomass gasification systems, scrubbers, venturiers, humidified packed beds. Methods for tar removal based on water and solvent scrubbing have been developed over the last decade. Processes using water generate a polluted stream difficult to dispose by economical methods. Methods using organic solvents have been proven to be efficient from the technical point of view; however, they are complex (when solvent recuperation is applied) or expensive (when simple scrubbing without solvent regeneration is applied). This reduces significantly its potential application in small and medium scale. Therefore, cost-efficient and simple methods for tar removal need to be developed for commercial implantation of the technology.

In the present work we explain tar removal by scrubbing, for this we propose to use an absorbing stream formed for 80% of tar generated in gasification process and 20% of additives for improve the properties. These properties can be: absorb capacity, viscosity and composition.

2 THE CONCEPT OF CAPTURING TAR WITH TAR

There are several classification of tars [3,7]. According to ECN classification tar class or families are classified in the following: tar class 1 is composed of very heavy tars that cannot be detected by GC-MS. Class 2 are heterocyclic compounds, mainly oxygenated and, to large extent, soluble in water. Tar classes 3, 4 and 5 are formed by aromatic compounds with 1, 2-3 and more than 4 aromatic rings respectively.

For the analysis that follows, a simplified classification of tars is adopted, by distinguishing two lumps: "heavy tars" and "light tars". Heavy tars include heavy aromatized tar, condensing at high temperature, so they have a strong influencing on the gas dew-point. Light tars are in higher concentration than heavy tars in the gasification gas. They include compounds such as benzene, toluene or indene, being capable to act as solvent to heavy tars at ambient temperature. Light tars also include some compounds that are, to some extent, soluble in water.

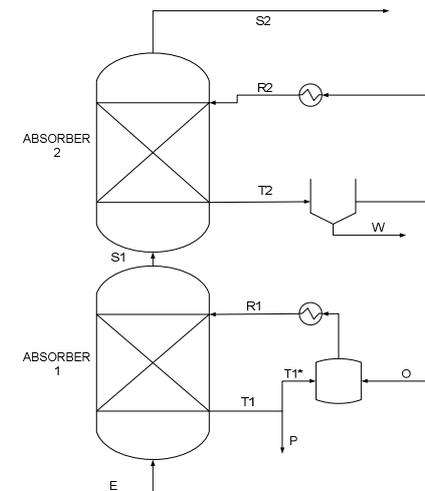


Figure 1: Shows the basic scheme of the absorber.

A proposal consisting of an absorption/condensation using light tar to remove heavy tar is proposed here. The main idea is to remove the heavy and light tars in two different stages: heavy tar is removed in a first absorber at higher temperature, whereas the light tar and moisture are removed from the gas in second stage at lower temperature. Water and light tars are separated, being this later recirculated to the first scrubber to be used as a liquid solvent with some external solvent addition. The solvent addition should be minimized in order to make the process feasible. The additional solvent depends on the capture efficiencies required and the flow properties of the resulting liquid streams. The key design consideration to achieve the above results is the control of temperature profiles in the absorber.

Table I: Operation point

T _{bed} (°C)	ER	Class 2 (mg/Nm ³)	Class 3 (mg/Nm ³)	Class 4 (mg/Nm ³)	Class 5 (mg/Nm ³)
765	0,27	1916	9783	2051	105
840	0,34	496	10510	2459	112

A diagram of the concept is presented in Fig. 1 where the main streams are shown. The temperatures in the diagram are illustrative of the targets to be achieved by proper design of the system as it is discussed below. In the absorber 1 the gas phase is cooled down, reducing its temperature from 450°C (E) to 75°C (S1). Common dew points on biomass gasification are between 140 and 160°C. In the first stage the gas phase becomes oversaturated in tar and condensation starts. Temperature in R1 is estimated to be 70°C and 100°C in T1 stream. In the second absorber gas is further cooled down to 20°C (S2). Temperatures in R2 and T2 are 15 and 50°C. The liquid flow rate is adjusted to achieve the required temperature drops. In the first absorber high liquid flowrate is needed due to the high temperature drop between the inlet and the outlet gas streams. In the second stage less cool liquid is needed since the temperature drop is only about 50°C. In this stage, in addition to capturing light tars, water is condensed. The water could dissolve part of heteroatomic tars and inorganic contaminants present in the gas. The effect of capturing inorganic contaminants such as NH₃, SH₂ or HCl could be beneficial for the end use of the gas but it will be a contaminated stream to treat. This mixture of aqueous-organic phase that is generated requires installing a decanter to remove the water condensed in the second absorber.

For the design of the concept proposed, it is necessary to estimate some properties of the liquid streams. In particular major impact on the design comprises the solid-liquid and gas-liquid equilibrium, i.e. the solidification and condensation temperature at the pressure of operation. In this communication the viscosity and the melting temperature of various liquid mixtures are investigated.

3 EXPERIMENTAL

The liquid mixtures are made synthetically in the lab to simulate potential mixtures that can be achieved in the system conceptualized above. The mixtures studied in are made of five selected tars. This is a simplification of real liquid to be obtained, where a complex mixture of tars, inorganic contaminants and solid particles will be obtained.

Previous samplings of the authors in pilot and demonstration FB gasifiers allow estimating the most representative tar compounds of the gas (following the classification of ECN): Toluene and indene for tar Class 3, naphthalene and phenanthrene for tar Class 4 and pyrene for tar Class 5. Table I presents a typical tar composition from previous experiences at demonstration plant. Relative mass proportions for tar Class 3 and 4 are, respectively, toluene/indene=2/1 and naphthalene/phenanthrene=4/1 [7]. On the basis of the melting temperatures of selected tars (see Table I) it is concluded that toluene and indene will act as solvent in both scrubbers, whereas phenanthrene and pyrene will act as solute. Naphthalene will be in liquid phase (solvent)

in the first scrubber, whereas it will behave as solute in the second one

Table II: Select characteristics of tars

Compound	Melting	Boiling
	Temperature (°C)	Temperature (°C)
Toluene	-93	111
Indene	-4	182
Naphthalene	80	218
Phenanthrene	99	340
Pyrene	148	448

Two types of tests were conducted to study the solubility and melting temperature as well as viscosity of the tar mixtures. The mixtures investigated are specified in Fig.2 (underlined area). The area studied includes mixtures of tar with higher proportion in class 4 and tar class 5 than those to be found in the liquid stream in the first scrubber. The viscosity of the mixtures 1, 3, 15 and 18 are studied as extreme cases of the values to be found in the real scrubber. T1 and R1 are streams with high concentration of heavy tars being the lowest temperature in the absorption tower 70 °C; therefore the viscosity of points 1 and 3 (heavy tar mixtures) was studied at this temperature. T2 and R2 are streams with high concentration of light tars; in this case the viscosity was obtained at 15 °C and 50°C.

3.1 Melting temperature of tar mixtures

First, the mixture is heated up to such a temperature that the mixture is liquid. This homogenization temperature is higher than the melting temperature due to the presence of pure crystals of the different tars. Then, the mixture is cooled down until room temperature. Thereafter, the mixture is slowly heated until T_{melt} (the solubility temperature) where the homogeneous mixture becomes liquid. The equipment used to study all mixtures is a thermostatic bath, where temperatures between -20 °C and 150 °C can be set. Finally two types of mixture were investigated: with and without bio-oil. 20% of bio-oil was used for the mixtures with bio-oil, a proportion above which the process is not economical feasible because of the high cost in solvent addition.

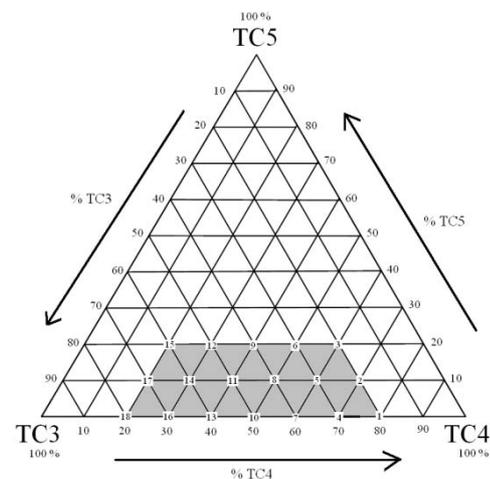


Figure 2: Zone indicating the composition of the mixtures tested in this work: TC3, TC4 and TC5 are % of mass of tar class 3, 4 and 5.

3.2 Viscosity of tar mixtures

Experiments were conducted to determine the viscosity of tar liquid mixtures at different temperatures. A ball viscosimeter immersed in a thermostatic bath was used. The absolute viscosity in centipoises is calculated using a Haake-Falling-Ball-Viscosimeter. The viscosity is determined applying the Hoeppler formula (1).

$$\gamma(\text{centipoises}) = t \cdot (\rho_{\text{ball}} - \rho_{\text{liquid}}) \cdot K \quad (1)$$

t being the time in seconds, ρ_{ball} and ρ_{liquid} are the mass density of ball and liquid in g/cm^3 , and K a characteristic constant of the viscosimeter ball used

4 RESULTS AND DISCUSSION

In Figure 3 the measured melting temperature is shown as a function of tar Class 4 for three proportions of tar class 5. Tar Class 3 is obtained by difference. Solid lines represent pure tar mixtures whereas the dotted lines

correspond to tar-biodiesel mixtures. It is concluded that for pure tar mixtures the increase of tar Class 5 (decrease on tar class 3 proportion) do not lead to a significant increase on the melting temperature. Furthermore the highest melting temperature measured (corresponding to the mixture TC3 20% / TC4 80%) is well below the lowest design temperature considered to be found in the first scrubber (70°C).

For the tar-biodiesel mixtures (dotted lines) significant differences are found in melting temperatures depending on the proportion of the tar Class in the mixture. The bio-diesel addition reduces the melting temperatures between 19 and 14 °C as light tars increase, whereas the presence of heavy tars only slightly decrease the melting temperatures. It is concluded that it is not necessary to add biodiesel to the first (hot) scrubber because no significant improvement on melting temperatures is achieved. However the decrease of the melting temperatures as increasing the light tar proportion is interesting in order to feed the liquid at temperatures below 20°C in the second scrubber.

Table III: Experimental data

Study point	TC3 (weight %)	TC4 (weight %)	TC5 (weight %)	T _{melt} (°C)	T _{melt} (°C) with 20% Biodiesel
1	20	80	0	53	51
2	20	70	10	48	44
3	20	60	20	45	38
4	30	70	0	47	
5	30	60	10	42	
6	30	50	20	38	
7	40	60	0	40	35
8	40	50	10	35	30
9	40	40	20	33	28
10	50	50	0	33	
11	50	40	10	31	
12	50	30	20	30	
13	60	40	0	29	15
14	60	30	10	26	12
15	60	20	20	25	9
16	70	30	0	23	
17	70	20	10	22	
18	80	20	0	20	1

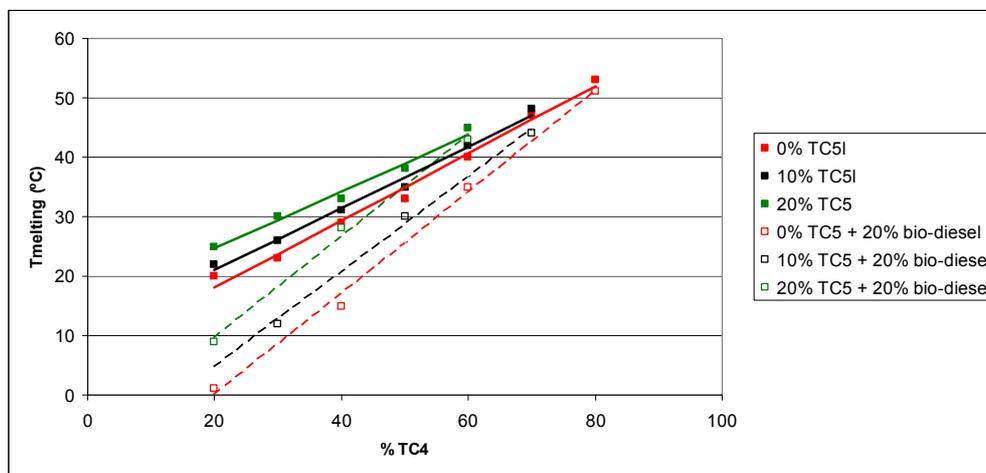


Figure 3: Melting temperatures of pure tar mixtures (solid lines) and tar-biodiesel mixtures (dotted lines)

Table 4 shows the viscosities of the pure tar mixtures 1, 3, 15, 18 at the temperatures indicated above, i.e. 15 and 50 °C for light tar mixtures 15 and 18, and 70°C for heavy tar mixtures 1 and 3. The higher viscosity measured is low enough to avoid pumping of flow problems.

Table IV: Experimental data of viscosity

Study point (figure 2)	Temperature (°C)	Viscosity (centipoises)
1	70	<0.5
3	70	<0.5
15	15	1.1960
15	50	0.7380
18	15	<0.5
18	50	<0.5

5 CONCLUSIONS

A new concept to remove tar from biomass gasification gas by scrubbing is presented. The concept deals with removing heavy tar in a first hot absorber, whereas the light tar and moisture are removed in second cold absorber. Water and light tars are separated, being this later recirculated back to the first scrubber, where it is used as a liquid solvent. Synthetic mixtures representing the liquid mixtures expected to be found in a scrubber running under the proposed concept were prepared and melting temperatures and viscosity were measured. Results suggest that the tars capture at high temperature will remain liquid and the viscosity of the liquid stream containing the heavy tars will not caused flow problems. However further investigation has to be made to assess the potential effects of inorganic pollutants and particles. Furthermore, it is necessary to avoid cool points in the liquid streams since fast nucleation and solidification were observed.

6 REFERENCES

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