

Comparison of Different Systems for Tar Removal for Renewable Energy Derivation from Biomass Gasification

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Abstract

The purpose of this study is to identify the fluid absorbent which is able to ensure satisfactory tar removal efficiency such as to minimize the impact of biomass gasification and renewable energy derivation on the environment and human health. Tar is a heterogeneous mixture in which exist hundreds of substances, both organic and inorganic. The absorption using washing fluids is the most widely used technique, at present, to remove contaminants in many gasification plants. The washing process, also known as process gas absorption, is an operation by which one or more contaminants contained in the flow of the gas are selectively absorbed into the absorbent material. However to ensure that the contaminant in the gas phase can be absorbed, it must have a certain solubility in the washing liquid. In the actual study, different absorbers are taken into account, including oil from food waste, water and nickel-mayenite catalysts (5 % vol. nickel) at two different operating temperatures (700 - 800° C).

Keywords: Gas; TAR removal; Biomass; Renewable energy; Biocatalytic gasification Ni-catalyst; Fuel; Tar

1. Introduction

Various are the renewable technologies but most are aleatory because dependent from solar, wind, geothermal or biomass [1, 2, 3, 4]. For this reason to be supplemented with other types of energies. One of the most important energy renew-

able sources is biomass a short chain [5, 6, 7] which is a carbon neutral energy source. Its role is considered as fundamental for the satisfaction of energy demand [8, 9]. Biomass can be used in thermo-chemical process, such as biocatalytic gasification, to obtain syngas to produce chemicals, biofuels, hydrogen for engine or fuel cell [10, 11], heat and electricity. Syngas is a gaseous mixture of hydrogen, carbon monoxide, methane, carbon dioxide, nitrogen, if air is used in the process, with eventual presence of contaminants such as sulfur and chloride compounds, solid particles, alkali metals and tars [12, 13]. So the use of syngas requires expensive gas cleaning systems to remove the contaminants, with particular attention to the presence of tar which causes limitations and difficulties in syngas use [14]. Tar is composed of condensable organic compounds and, depending on the temperature, it is possible to contain primary oxygenated products, heavier deoxygenated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) [5]. In general, by means of gasification process, hundreds or even thousands of different tar species can be generated, depending on to the type and design of gasifier, the operating process parameters such as temperature, pressure, type and amount of oxidant, residence time of biomass and type of biomass and its impurities [15,16].

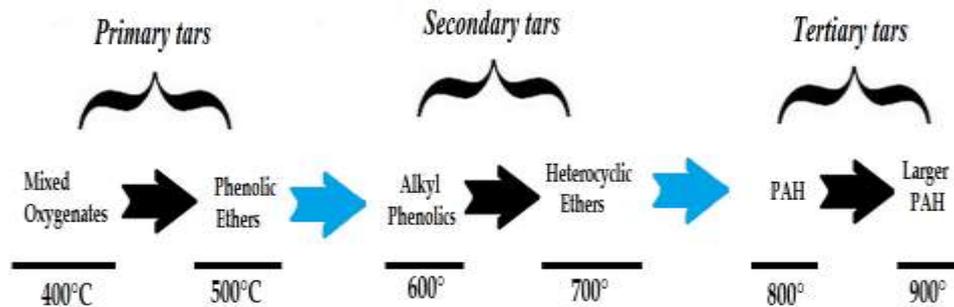


Figure 1. Tar evolution in function of the temperature [14]

Nowadays, different methods are available to reduce the tar content of syngas such as physical treatment, thermal cracking or catalytic reforming that is characterized by a fast reaction rate and reliability in addition to improving the quality of the syngas in terms of carbon monoxide and hydrogen content [17]. Referring to the use of catalysts for tar removing, it is possible have different type of materials to use and two methods: one in case of insertion of catalyst inside the reactor of gasification and the other in case of treatments downstream the reactor [18].

Between the catalysts that can be used to clean the syngas from tar there are the calcined rocks, zeolites, iron ores, alkali metals, noble metals and nickel-based catalysts. This last category of catalyst is considered the most promising for tar removal and syngas reforming. Nickel-based catalysts can be supported by metal oxides such as alumina and magnesium oxide or natural materials such as dolomite, olivine, activated charcoal. Anyway is important to consider that these

supports are expensive, and the phases of the catalyst preparation need of time and energy, so this is a problem for a large scale application of nickel-based catalysts [19]. It is also important to consider that they could improve their removal tar efficiency if used as in-bed material, but with consequences of a rapid degradation and a contamination of ashes obtained from the biomass gasification [18]. Another important aspect is that nickel-based catalysts could be subject to sulfur poisoning depending on the operating condition of the process with particular reference to the temperature parameter [20]. In this sense an important alternative could be the char-supported catalysts that are less expensive and that are characterized by an energy recovery as consequence of the gasification of the char [21, 22].

So, as is evident from what was said above, the clean syngas is an important aspect on which depends the quality of the gas and therefore the possibility of its use. With particular reference to the removal of tar, there are several possibilities of intervention and in this work is proposed a study concerning the removal of tar at low temperature through a catalyst consisting of nickel and mayenite placed downstream of the particulate removal system.

2. Experimental

The efficiency of TAR removal from syngas, is studied in relation to: the use of a catalyst composed by nickel (5 % in vol.) and mayenite (95 % in vol.), respectively, at a temperature of 700 °C and 800 °C, the use of a fluid absorber used oil feed and use of fluid absorbing water. The system of syngas production is characterized by a fluidized bed gasifier fed with *Corylus avellana* shells and steam as oxidizing agent, a the cyclone for removal of char, a ceramic filter for the removal of particulate and scrubbers, working at low temperature, for the capture of the TAR by means condensation and absorption methods.

Table 1 shows the chemical and physical characterization of the *Corylus avellana* shells used in the gasification process.

Table 1. Characteristics of hazelnut shells

Parameter	Value	U.M.
Moisture	12,80	% (w/w)
Ash	0,86	% (w/w dry)
Volatile matter	74,40	% (w/w dry)
C	51,00	% (w/w dry)
H	6,10	% (w/w dry)
N	0,45	% (w/w dry)
O	41,50	% (w/w dry)
LHV	18,01	MJ/Kg dry
HHV	19,50	MJ/Kg dry

In Table 2 are shown the operating parameters referring to the biomass process gasification.

Table 2. Operating parameters

Parameter	Value	U.M.
Biomass flow	345,6	g/h
Steam flow	276,5	g/h
Reactor temperature	850,0	°C

With regard to the efficiency of TAR removal from syngas, were performed 5 tests, in particular: a "white" test without the use of catalyst or adsorber fluid, two tests with use of the catalyst at a temperature of respectively 700 °C and 800 °C, a test with food waste oil as a fluid adsorber and a test with water as a fluid adsorber. For the sampling of the TAR methods have been used for condensation and absorption. The sampling phase is based on the use of a system of bubblers, with different configurations for each test (Figure 2), places within a system filled with coolant (ethylene glycol solution) at a temperature of -10°C, which have the purpose to carry out the condensation of TAR and, through the presence of a solvent, the absorption of the same. In particular, the syngas produced, before being analyzed by gas chromatograph, was made to flow in the system consists of four bubblers of which the first three filled each with 50 mL of acetone, the solvent in which is dissolved the TAR, while the fourth bubbler operates without any inner solvent.

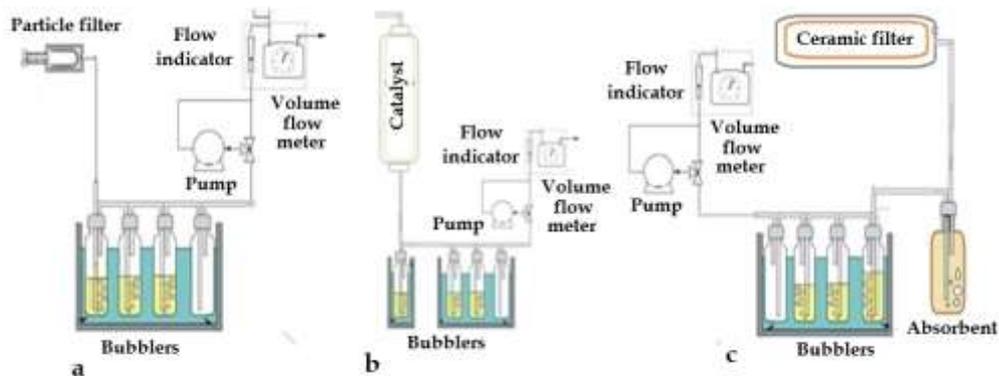


Figure 2. Global tests configurations: (a) white test. (b) test with catalyst. (c) test with fluid adsorbent (water and food waste oil)

Referring to use of water for TAR removal, it was analyzed by GC-MS the water solubility of different TAR compounds (Table 3).

Table 3. Water solubility of the compounds of the TAR

Compound	Molar mass	Solubility in water (mmol/L)	Solubility in water (mg/L)
Phenantrene	178,24	0,00130	0,23
Anthracene	178,23	0,00037	0,07
Pyrene	202,26	0,00072	0,15
Napthalene	128,17	0,24000	30,76
Styrene	104,15	2,30400	240,00
Xylene	106,16	0,00000	0,00
Toluene	92,14	5,52300	520,00
Benzene	78,11	22,66000	1770,00

From the Table 3, it is evident that phenol is the pollutant that has the best features of solubility in water (about 84 g/L), polycyclic aromatic hydrocarbons typically have very low solubility in water or anything while the derivatives of benzene and benzene present discrete solubility between 0,2 to 1,8 g/L. The water is the washing fluid that is more commonly used in gasification systems, however, since the tar has poor solubility in water has been studied use of food waste oil that on the contrary [23,24] ensures greater efficiency of absorption of the TAR. In particular, through the use of water is possible to remove a little over 30 % of the tar while by the use of oil of plant origin can be up to an efficiency of removal of the TAR of about 60,4 %. In detail, the removal efficiency is decreasing switching from diesel to vegetable oil, biodiesel, oil machinery until to the water.

3. Results and discussion

3.1 White test

Obtained syngas was flowing within the system of bubblers in order to collect the tar which was formed during the gasification tests and was subsequently analyzed by the gas chromatograph 'Agilent GC 7890' to obtain the composition (Table 4). Through gas chromatograph, the composition of the TAR contained in the gas was also determined (Table 5). Results show that the predominant class of TAR is the third that is formed by light aromatic hydrocarbons characterized by a single ring (including toluene, benzene, xylene and styrene).

Table 4. Syngas composition

Compound	H₂	CO	CH₄	CO₂
% vol.	51,68	23,36	5,6	19,36

Table 5. TAR composition

Compound	Class	mg/L	g/Nm ³
Phenantrene	4	10,94	0,066865874
Anthracene	4	10,99	0,067171477
Pyrene	5	3,12	0,019069610
Naphtalene	4	635,50	3,884210526
Styrene	3	33,78	0,206465195
Xylene	3	178,76	1,092590832
Toluene	3	782,92	4,785249576
Benzene	3	2895,85	17,69959253

3.2 Catalyst test

For the test, 15 mL of a catalyst composed of nickel and mayenite of which 5 % vol. nickel was used. The catalyst was placed inside the plant downstream of the dust removal and later tests were carried out at two different operating temperatures (800 °C and 700 °C). In the first case it has been possible to record an increase of hydrogen and carbon dioxide of about 5 - 6 % compared to the white test, while in the second case, an increase of about 10 % was observed. Referring to the TAR content, in Table 6 are shown results about TAR composition in case of use of catalyst for two different operating temperatures.

Table 6. TAR composition

Compound	mg/L (T = 800 °C)	mg/L (T = 700 °C)	g/Nm ³ (T = 800 °C)	g/Nm ³ (T = 700 °C)
Pyrene	0,47	1,12	0,0028	0,0072
Phenatrene	2,67	2,30	0,0158	0,0168
Anthracene	0,70	0,76	0,0040	0,0048
Benzene	512,64	854,54	3,0725	6,0578
Xylene	0,68	3,85	0,0035	0,0265
Toluene	69,29	66,64	0,4158	0,4690
Styrene	0,62	3,84	0,0033	0,0263
Naphtalene	96,77	224,28	0,5815	1,5645

The results of TAR removal or conversion efficiency η (Formula 1) are shown in Table 7:

$$\eta = \left(\frac{\text{white test concetration} \left[\frac{mg}{L} \right] - \text{test concentration} \left[\frac{mg}{L} \right]}{\text{white test concetration} \left[\frac{mg}{L} \right]} \right) \times 100 \quad (1)$$

Table 7. Efficiency TAR removal

Compound	H (T = 800 °C)	η (T = 700 °C)
Pyrene	84,94	64,10
Phenatrene	75,59	78,98
Anthracene	93,63	93,08
Benzene	82,30	70,49
Xylene	99,62	97,85
Toluene	91,15	91,49
Styrene	98,16	88,63
Naphtalene	84,77	64,71

From the results obtained it is clear that the conversion efficiency of the TAR is greater in the case in which the catalyst operates at a higher temperature, 800 °C instead of 700 °C. In the first case the efficiency of removal are for all the compounds more than 80 %, and for most of the compounds above 90 %. In the second case the efficiency amounted less than 90 %. In both cases there is a greater removal efficiency relatively to the compounds of third class: xylene and styrene.

3.3 Water test

The water test is characterized by a system with five bubblers (Figure 2c) with the first of these placed after the ceramic filter and filled of water at room temperature. In table 8 are shown the results about the TAR composition and TAR removal in case of use of water as fluid absorber.

Table 8. TAR composition and removal efficiency for water test

Compound	Class	mg/L	g/Nm³	η
Phenatrene	4	2,65	0,0248	75,78
Anthracene	4	1,63	0,0153	85,17
Pyrene	5	0,46	0,0038	85,26
Naphtalene	4	10,72	0,1002	98,31
Styrene	3	16,46	0,1558	51,27
Xylene	3	17,96	0,1714	89,95
Toluene	3	580,25	5,5226	25,89
Benzene	3	1312,61	12,474	54,67

The results of the analysis (Table 8) shows that the water has a less effect on the compounds of the third class except to the xylene. Relatively to the compounds of

the fourth and fifth class, it is possible to note that in both cases the water acts effectively. In particular regard to the fourth class, use of water shows satisfying absorption values in consequence of condensation of the TAR.

3.4 Food waste oil test

For the test, it was used a food waste oil, in particular exhausted frying food oil, filtered and purified from the residue from coarse with a density of 1.053 g/ml. The system used for the test is constituted by five bubblers (Figure 2c) with the first of these placed after the ceramic filter and filled of 200 ml of oil at room temperature. In table 8 are shown the results about the TAR composition and TAR removal.

Table 9. TAR composition and removal efficiency for food waste oil test

Compound	Class	mg/L	g/Nm³	η
Phenantrene	4	4,4	0,0349	59,78
Anthracene	4	2,87	0,0222	73,89
Pyrene	5	0,77	0,006	75,32
Napthalene	4	2,81	0,0217	99,56
Styrene	3	4,91	0,0383	85,46
Xylene	3	16,33	0,1278	90,86
Toluene	3	383	3,0008	51,08
Benzene	3	757,16	5,9318	73,85

4. Conclusions

The technology that ever showed the best performance and most reliable is the catalyst operating at a temperature of 800°C. However, among the disadvantages in the use of the catalyst are: the catalyst deactivation due to sulfur, chlorine and alkali metals; coke formation (for high levels of tar); the sintering of the nickel-based catalyst due to repeated cycles of thermal regeneration at high temperature; the costs associated with the consumption of catalyst and the need for disposal of the exhausted catalyst. Regarding studies carried out on fluids absorbers one can conclude that the concentration of tar in time within an absorber is a function of the nature of the absorber and of the characteristics of the individual compound present in the tar. The water showed satisfactory removal features that are related in large part to the condensation, due to the low operating temperatures of the fluid, the more that the actual absorption capacity because most of the components of the tar have low or no solubility in water. The use instead of an absorber oil produces greater efficiencies of removal of non-polar substances and in general has the removal efficiencies comparable with those resulting from the

use of catalytic cracking (removal efficiency of total of approximately 67% compared to 33% water). According to studies carried out here it can be concluded that the oil is the absorber that has the characteristics of absorption efficiency more profitable. Unlike water, which requires following the operation of absorption of the purification treatment, the oil can, following its use, be reused as fuel within the gasifier in addition to the same biomass or transferred to another system with a significant reduction in the cost of disposal and treatment.

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