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Process Simulation of Tar Removal from Gasification Producer Gas

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Biomass gasification is being regarded as an efficient process for the production of heat and power and even for the conversion of biomass into biofuels. Its main drawback is the non-negligible tar formation within the process. As the producer gas temperature decreases in the downstream equipment, tar will condense leading to the fouling, blocking of engines, filters and turbines or catalyst deactivation. The challenge is to remove/reduce tar in the product stream. An oil-based gas washing process (OLGA), combining a collector with an absorber and a stripper, is one of the most adapted processes for tar removal. In this work, simulations were conducted using Aspen Plus. These simulations helped in assessing the efficiency of the process in reducing the tar content for an initial concentration of 7,098 mg/Nm^3. The variation of the tar reduction efficiency was studied as a function of the oil flow rate and temperature to validate the simulated data by the experimental one. Results showed that equal overall tar reduction efficiency, of 98.8 %, was achieved for an oil flow rate of 5,500 kg/h at 333 K. However, certain deviation was faced while comparing the elementary tar content reduction. Excluding the light tar components, mainly benzene and toluene, led to this high removal efficiency. By adding those components to the simulations, the tar removal efficiency was reduced to 57.6 %. This work focuses on a large assessment of existing processes and perspectives, in particular the removal of the lightest tar components.

1. Introduction

Shifting from non-renewable energy to renewable energy sources is a key factor in reducing carbon dioxide emissions and limiting climate change. Biomass has been recognized as an important source for renewable energy and its gasification is one of the most promising technologies for its conversion into bioenergy and biofuels. Gasification yields a gaseous product called producer gas in addition to impurities. The gas can be further processed to produce heat and electricity through combined heat and power (CHP) generation units or to produce transportation fuels via Fischer-Tropsch (FT) or bio-methane via methanation reactors. Carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), steam (H_2O) and nitrogen (N_2) are the major components of the producer gas in addition to tar vapors and ashes (Amaral et al., 2019). Other than the producer gas composition, impurities produced during biomass gasification, especially tars, require additional treatment before upgrading the producer gas. The tar content after biomass gasification varies between 1 g/Nm^3 and 100 g/Nm^3. If not removed, as the temperature decreases in the downstream equipment, tars will condense and lead to plugging, fouling engines, turbines and filters. For CHP units, the tar content, excluding the lightest tar fraction formed mainly of benzene, toluene and xylene (BTX), should be reduced to 5 mg/Nm^3 (Anis and Zainal, 2011). While for FT and methanation, the tar content, including BTX, should be reduced to 1 mg/Nm^3 (Woolcock et al., 2013). Otherwise, tars will be decomposed into coke in the catalytic reactors leading to catalyst deactivation (de Lasa et al., 2011). The production of heat and power based on biomass gasification is well developed and several methods for tar removal fulfil the gas specifications. While coupling it with a chemical synthesis process involving catalysts is still quite limited due to the low tar content required. The existing methods for tar removal can be divided into two groups: primary and secondary (Valderrama Rios et al., 2018).

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Figure 1 summarizes the different methods used for tar removal. Primary methods are based on reducing the tar formation within the gasifier by varying its operating conditions, or by changing its design. However, even when primary methods are applied, the need of secondary methods is inevitable for a complete removal of tars downstream the gasifier (Bergman et al., 2002).

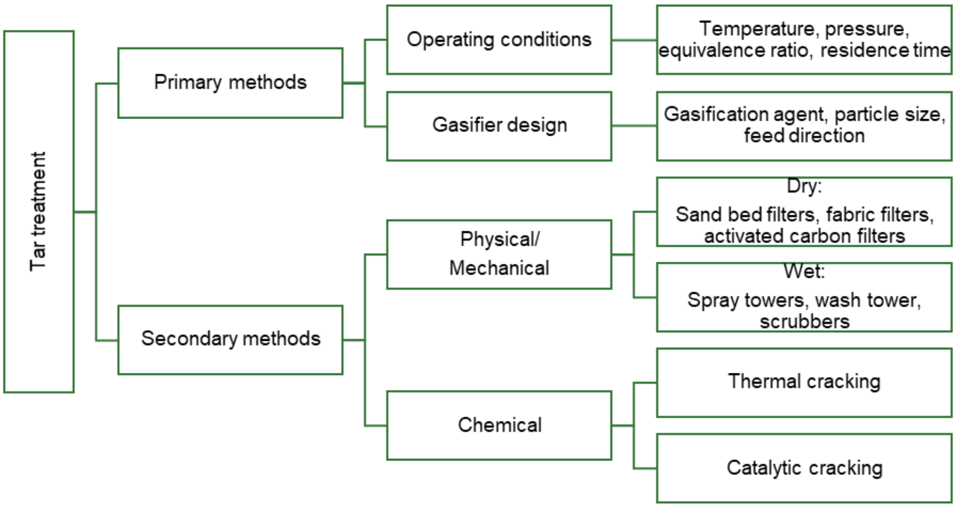

Figure 1: Schematic illustration of the different methods used for tar treatment

Scrubbers are the most suitable units for small-scale applications (Lotfi et al., 2019). Their main disadvantage is the generation of contaminated water or oil by exchanging the tar problem from the vapour phase to the liquid one. Several studies were conducted on the scrubbers. Water, biodiesel fuel, diesel fuel, engine oil and vegetable oil, were evaluated as scrubbing mediums to compare their scrubbing efficiency (Phuphuakrat et al., 2011). Among them water has the lowest removal efficiency, while biodiesel fuel has the highest one. Experimental setup showed that the tar removal is affected by the absorbent flow rate more than the absorbent temperature (Lotfi et al., 2019). One of the most efficient scrubbing methods is named OLGA. It was developed by the Energy research Centre of the Netherlands (ECN) and it combines two oil scrubbing columns with a stripper for oil regeneration (Meijden, 2014). OLGA, targets the selective tar removal while avoiding the water condensation. This eliminates the generation of a waste stream containing a mixture of tar and water (Rabou et al., 2016). For this purpose, the gas inlet temperature is kept higher than the tar dew point (593 K – 623 K) and the exit gas temperature should be kept higher than the water dew point (333 K – 373 K).

Available information on the operating conditions and the liquid used in the columns is rare. This work targets developing simulations of OLGA using Aspen Plus V8.8. in order to study the impact of the absorbent flow rate and its temperature on the removal efficiency by tar classes, including BTX components. The three columns were developed based on equilibrium stage model at atmospheric pressure and for a gas flow of 4,000 Nm^3/h.

2. Models and methods

2.1 Process description

The process is simulated using Aspen Plus to study the parametric impact on tar removal efficiency while considering the energy consumption. Figure 2 depicts the flowsheet of the process. The gas is being cooled in the first section (COLECTOR) by the means of scrubbing oil. As a result, heavy tars (class 5 and most probably class 1) are being condensed in the collector. The collected heavy tars and particles are separated and injected in the gasifier (TO-GAS). The rest of the liquid stream (OIL-REC1) is recycled back to the collector after being cooled to its initial temperature. In the second section (ABSORBER), light tars are absorbed in the scrubbing oil by changing the operating conditions. The oil is then regenerated in the third column (STRIPPER) using air or steam and recycled to the absorber. The stripping air charged with light tars is recycled back to the gasifier and acts as the gasifying agent (Boerrigter et al., 2005). The saturated stripping oil leaving the absorber (OIL-OUT2) and the regenerated scrubbing oil leaving the stripper (OIL-CL2) exchange heat. The rest of cooling and heating is added by cooling water and steam. Operating at optimum conditions of temperatures and scrubbing oil flow rates, reduces the concentration of tar from7 g/Nm^3 to 50 mg/Nm^3 by excluding toluene from the analysis. Heavy tars (class 5) where completely removed, naphthalene was reduced by 99.5 % and phenol by 85 % (Boerrigter et al., 2005).

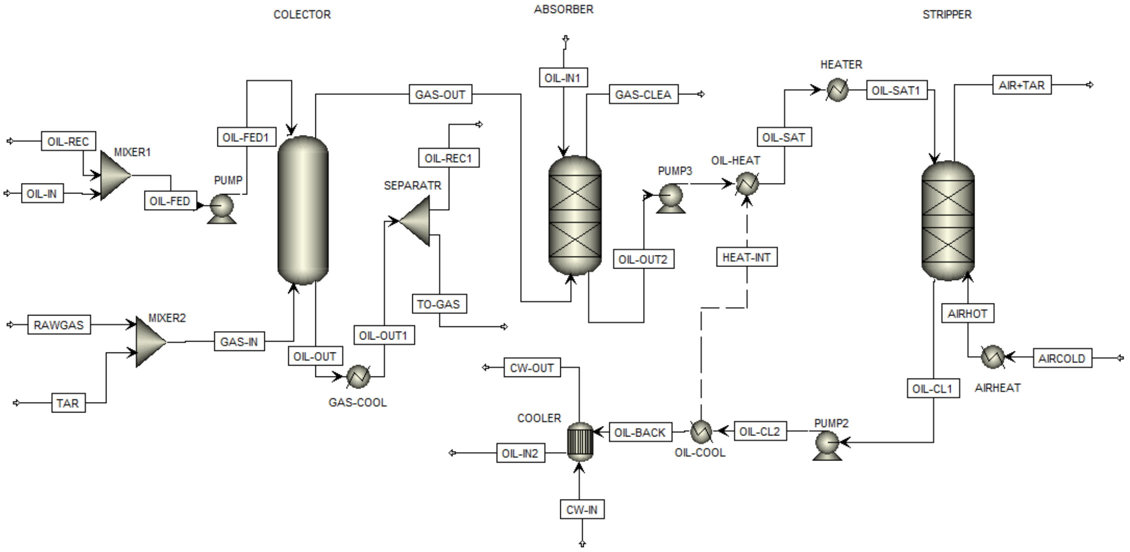

Figure 2: Schematic diagram of OLGA process using Aspen Plus

2.2 Model paramaters

The three columns where simulated as RadFrac columns based on equilibrium stage model. The selected liquid stream for the collector and the absorber is the methyl-oleate. The latter was selected for having similar composition and properties to the rapeseed methyl ester (RME) that is usually used for tar scrubbing. The adapted composition of the producer gas, shown in Table 1, was retrieved for a Danish straw circulating fluidized bed (CFB) gasifier using air as a gasifying agent (Zwart et al., 2010). The initial tar content (TAR) is presented in Table 2. SR-POLAR was selected as the physical property method for the simulations since it is appropriate for polar compounds, in combination with light gases. The gas enters the first scrubber at a temperature of 623 K while methyl-oleate was fed at 298 K. In the collector, tar is being removed by condensation and not by absorption since the scrubbing medium becomes saturated after a certain time of operation. While for the absorber, methyl-oleate is being regenerated continuously in the stripper.

Table 1: RAWGAS stream composition (Zwart et al., 2010)

	H_2	CO	CO_2	CH_4	N_2	H_2O	C_2H_y	C_6H_6	C_7H_8
Vol %	2.86	13.30	11.83	3.51	48.14	18.40	1.38	0.5	0.08

The conditions for the pumps, coolers and heaters were deduced from (Boerrigter et al., 2005). The latter stated that the total operating cost was equal to 1.1 €/t of biomass. This cost is divided into 26 % for electrical consumption, 8 % for cooling, and 66 % for steam consumption. Calculations of the energy consumption was done by considering that the syngas yield is equal to 1.3 Nm^3/kg of biomass, the price of cooling water is equal to 0.1 €/m^3, the price of electricity is equal to 0.07 €/kWh$_e$, and the price of heat is equal to 4 €/GJ. The price of the lost scrubbing medium during the operation is equal to 9 €/t of biomass, and the price of the scrubbing medium is equal to 2 €/L. Toluene and benzene were excluded from the tar content accounting.

3. Results and discussion

In the first column, the total tar content was reduced by 28 %. Only heavy tars (class 5) were removed in the collector by reducing the temperature of the gas. As seen in Table 2, 99.97 % of the heavy tar components was removed in the first column. The gas enters the second column at a temperature of 341 K. Several constraints should be considered while designing the second column. First, as mentioned by (Zwart et al., 2010), the dew point of water for a content of 18.4 vol % is equal to 334 K. The temperature of the gas stream leaving the absorber should be kept higher than 334 K. Second, for a gas flow rate of 4,000 Nm^3/h, the energy consumption for the pumps, heaters and coolers should be equal to 8.17 kW, 101 kW and 1.78 m^3/h of cooling water.

The optimal operating conditions leading to a tar content similar to the experimental results found in the literature (Boerrigter et al., 2005) was achieved for a flow rate (OIL-IN1) of 5,500 kg/h and a temperature of 333 K. A comparison between the simulated results and the experimental ones retrieved from literature is then conducted and summarized in Table 2. The total tar reduction efficiency is similar for both cases, and it is equal to 98.8 %. However, a deviation between the simulated and the experimental elementary tar removal efficiency was noticed. The simulation showed that all the components heavier than naphthalene were totally removed. The components remaining in the gas phase were xylene and styrene, which are the lightest ones, in addition to a small amount of phenol, indene and naphthalene. For the experimental results, an important amount of phenol, naphthalene and quinoline remains in the gas phase, in addition to some heavy tar components such as phenanthrene. The deviation between the results might be caused by different operating conditions or the use of another scrubbing liquid, different gas solubility. The predicated behaviour was that of the simulation, since by decreasing the temperature, the heaviest tar components will be scrubbed first. Yet, in the experiment this statement was not validated. More details regarding the order of tar components condensation and phase equilibrium can be found in (Harb et al., 2020). The solubility of the gas components in the selected absorbent might affect the order of tar removal. The main tar components that were affected by the solubility are: phenol, xylene, styrene, naphthalene and quinoline. For the lightest components, xylene and styrene, their solubility in the absorbent used in the experiment was higher than that in the simulation. This reduced their removal efficiency in the simulation by 8.5 %. While for phenol, naphthalene, and quinoline, they might have a higher solubility in the absorbent used in the simulation than in the one used in the experiment. Their individual removal efficiency was increased by 2 %.

Table 2: Summary of the different tar concentrations in the gas phase within OLGA process for T = 333 K and $m_{methyl\text{-}oleate}$ *= 5,500 kg/h*

Tar Components	TAR mg/Nm^3 (Boerrigter et al., 2005)	Present work collector out GAS-OUT mg/Nm^3	Experiment out mg/Nm^3 (Boerrigter et al., 2005)	Present work out GAS-CLEAN mg/Nm^3
Ethylbenzene	7	7	0	1
m/p-Xylene	110	110	0	12
o-Xylene + Styrene	784	784	3	67
Phenol	173	173	24	2
o-Cresol	3	3	0	0
Indene	813	813	0	1.2
m/p-Cresol	6	6	0	0
Naphthalene	2,455	2,455	16	0.06
Quinoline	18	18	14	0
2-Methylnaphthalene	239	239	0	0
1-Methylnaphthalene	170	169	3	0
Diphenyl	88	40	0	0
Ethylnaphthalene	285	78	6	0
Acenaphthlalene	416	8	0	0
Fluorene	198	0.78	0	0
Phenanthrene	552	0.35	11	0
Anthracene	147	0.07	0	0
Fluoranthene	130	0.03	4	0
Pyrene	178	0.01	5	0
Benzo(a)anthracene	64	0	0	0
Chrysene	81	0	0	0
Benzo(b)fluoranthene	59	0	0	0
Benzo(e)pyrene	122	0	0	0
Total	7,098	5,118	86	83.26

To study the impact of the temperature and the flow rate of the scrubbing liquid on the process efficiency, two sensitivity analyses were completed. Both analyses were conducted to check the impact on the temperature of the gas stream leaving the absorber (GAS-CLEA) and the mass concentration of the main tar components remaining in the gas phase. The first study, illustrated in Figure 3, access the effect of the variation of the methyl-oleate mass flow rate for an inlet liquid temperature of 333 K. Figure 4 illustrates the second case studying the impact of the methyl-oleate temperature for a liquid flow rate of 5,500 kg/h. It can be observed in Figure 3 that increasing the flow rate increases the removal efficiency of each tar component. It can also be noticed that the concentration of the heaviest tar fraction will be reduced before the lightest ones for all the values of flow rate. The behavior is similar to that discussed previously. Contrary to the tar content, the temperature of the gas stream leaving the absorber (T out) is not importantly affected by the variation of the mass flow rate. The variation of the temperature is limited to 2.5 K. At high flow rate, even that the water is insoluble in the selected scrubbing medium, some water will be mixed with the absorbent. This could be explained by the low solubility of water in toluene and in benzene as well. By increasing the absorbent flow rate, more benzene and toluene are being condensed. This leads to increase the amount of water that could be dissolved in the condensed volume of liquid toluene and benzene. According to Figure 4, the liquid temperature has a high impact on T out. It can be deduced that, for a flow rate of 5,500 kg/h, the liquid temperature should be kept higher than 329 K to avoid steam condensation. Figure 4 reflects that the lower the liquid temperature, the higher the tar removal efficiency. The optimum condition is to operate at a temperature slightly higher than 329 K to ensure a high tar removal without mixing water with oil.

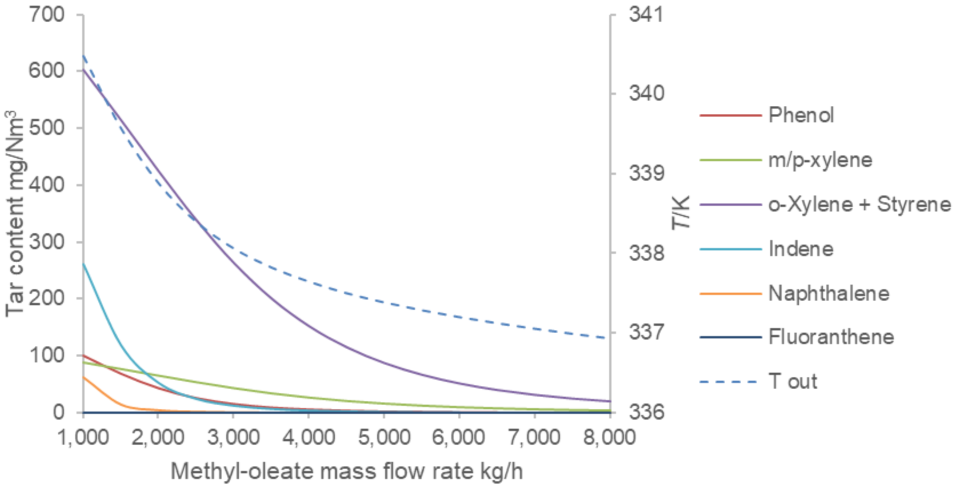

Figure 3: Variation of the tar content in mg/Nm^3 and the temperature in K of the gas leaving the absorber as function of the fed oil flow rate in the absorber at 333 K

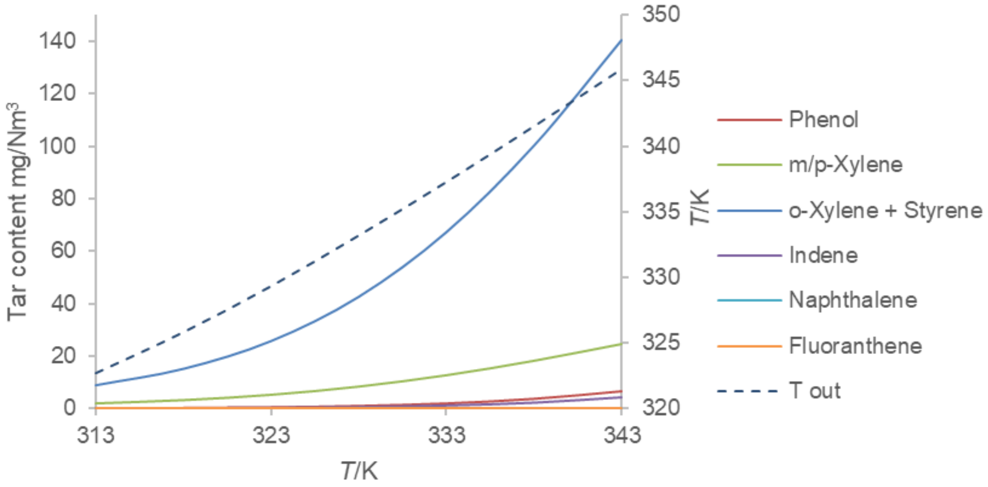

Figure 4: Variation of the tar content in mg/Nm^3 and the temperature in K of the gas leaving the absorber as function of the temperature of the oil fed to the absorber for a flow rate of 5,500 kg/h

This process is appropriate if the producer gas is used for CHP generation. However, if the producer gas is integrated in biofuel production, such as methanation, the catalyst will be deactivated by the remaining fraction of BTX that in other works are not considered as residual tar content. In the case where those benzene and toluene are considered, the overall tar removal efficiency of the process will drop from 98.8 % to 57.6 %. In particular, the reduction rate of benzene and toluene is equal to 36.7 % and 72.8 %. Even by changing the operating conditions, the removal efficiency was still low for feeding the producer gas to chemical synthesis processes. In order to reduce the BTX content, an additional stage of tar treatment is required. Usually a catalytic cracking step is added or a series of activated carbon beds (Thunman et al., 2018) is used in order to reduce the BTX content.

4. Conclusions

In this work, simulations for two stages tar removal scrubber were completed using Aspen Plus. It showed that the tar content was reduced from 7,098 mg/Nm^3 to 5,118 mg/Nm^3 in the first stage. Then to 83 mg/Nm^3 in the second one for a liquid flow rate of 5,500 kg/h and a temperature 333 K. The heaviest tar fraction, heavier than quinoline, was totally scrubbed. The removal efficiency of indene and naphthalene was higher than 99 %. The phenolic compounds were reduced by 98 %, while the lightest tar fraction, xylene and styrene, had the lowest removal efficiency (91 %). In order to achieve higher reduction rates, a higher flow rate with a lower temperature is required. The latter leads to the condensation of water vapor in the producer gas and to the generation of new waste water stream. The simulation shows that the achievable tar concentration remaining in the producer gas is suitable for CHP generation rather than synthetic fuels production. The latter involves within the production process several catalysts that are subject to deactivation by carbon deposition. Unsaturated hydrocarbons including the light fraction of tar, mainly benzene, toluene and xylene, forms a precursor for soot formation even at low content. For a sustainable operation, the tar content, including BTX, should be reduced to 1 mg/Nm^3. A solution for effectively removing BTX components could be their condensation at low temperature.

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