DECOMPOSITION OF TAR MODEL COMPOUND TOLUENE BY TREATMENT WITH THE HIGH-TEMPERATURE HYDROGEN/OXYGEN FLAME

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ABSTRACT: A complete decomposition of all organic molecules generated as a result of biomass gasification into simple inorganic species like CO and H_2 (syngas) means both an improved energy efficiency and technological robustness of the process of renewable synthesis gas (syngas) production. The syngas could be then converted into synthetic fuels, chemicals or electricity. A contamination of the produced syngas with polyaromatic hydrocarbons (PAH) promotes an origination of tar which, when the temperature of the gas becomes lower, deposits on the inner surfaces of the downstream equipment inducing its fouling and possibly its failure. A non-catalytic method of tar decomposition includes mixing of gasification products with plasma gas (usually air) generated by its heating to extremely high temperatures (5000^0C and higher) in a high-voltage electrical field. Combustion products at temperatures of the oxy-fuel flames could be also considered as plasma due to a presence of ionized particles, radicals and free electrons. The effect of continuous injection of the hydrogen/oxygen high-temperature flame into the blend of gases containing toluene in order to decompose the latter has been studied in the present work. Toluene in the mixture with nitrogen and steam (reaction mixture) was selected as a tar model compound because it has been regarded by many researchers as a precursor of heavier polyaromatic compounds in high temperature gasification processes. The experimental results indicate that treatment of the reaction mixture with the stoichiometric hydrogen/oxygen flame leads to the reforming of toluene into H_2 and CO. A certain excess of oxygen in the flame promotes almost complete toluene decomposition into syngas in the regime of its partial oxidation. In spite of some reduction in the amount of syngas produced, that excess oxygen in the hydrogen/oxygen flame could be efficiently applied to the syngas contaminated with tars; this allows the original syngas heating value to remain unchanged. A mechanism of hydrogen/oxygen flame influence on tar destruction/decomposition pathways is also discussed. Hydrogen and oxygen could be technically produced by electrolysis of water. The efficiency of electricity utilization to make the hydrogen/oxygen flame in order to decompose volatile organic compounds and tars will be a subject for our following studies.

Keywords: bioenergy, thermochemical conversion, tar, syngas, hydrogen, combustion

1 INTRODUCTION

Unlike ethanol production from biomass via fermentation, gasification technologies seem to be more flexible for allowing conversion of various carbonaceous materials (biomass, coal, industrial and household wastes) into a mixture of hydrogen and carbon monoxide (syngas) for the production of heat, power, liquid fuels and other chemicals. Further advancement for both technologies has been limited by an absence of a regular and reliable feedstock, taking into account that an economic competition on edible resources is highly undesirable.

The organic household and industrial (waste wood) wastes coming from big and middle-size cities could be considered a steady supply of carbonaceous feedstock, but it is often landfilled in spite of possessing a substantial heating value. This heating value can be utilized through its combustion (incineration) to produce steam for use as the working fluid of a power generation unit. However, that combustion is associated with formation of significant volumes of harmful pollutants (dioxins, furans, heavy metals, *SOx*, *NOx*, and etc.) and, therefore, requires a meticulous purification of flue gases [1]. Gasification and pyrolysis both imply thermal treatment of a carbonaceous solid material to obtain a combustible gas as an intermediate step in the further processing (e.g., electricity, fuel or chemicals production). An introduction of such intermediate step gives an opportunity to purify the gas before its further utilization. A presence of a regular feedstock to be reliably converted dictates some shift from a compact unit (gasifier) to an intellectual industrial technology where versatility and robustness, capacity and energy efficiency, environmental impact and safety are fundamentally accounted for.

With increasing temperature to 500-700^0C a sample of solids like waste wood, cardboard, textile releases volatiles that comprise about 70% of its initial weight and possess about half of its calorific value [2]. These volatiles represent a gas mixture which at standard conditions (P=1atm., T=298K) could be separated into organic liquids, water, and gases like CO_2, CO, H_2, CH_4, C_xH_y (x=2,3). In order to convert all different natural organic compounds by means of their complete thermal cracking and decomposition into CO and H_2 (syngas), the temperature of volatiles should be raised to higher than 1000^0C. The rise in temperature is usually achieved by an adiabatic combustion of some part of the produced syngas by adding a controlled amount of oxygen or air.

That combustion can be greatly promoted by mixing with an externally generated hot plasma gas (thermal plasma) that is partly composed of excited molecules, free electrons, ions, and radicals. The plasma gas is produced in plasma torches where the gas is heated to about 5000^0C along with passing trough the gap between high-voltage electrodes. Different kinds of organic wastes, varying from plastic and used tires to agricultural residue and medical waste, have been subjected to thermal plasma assisted pyrolysis and gasification tests in laboratory and pilot scale projects [3, 4].

An increase in the temperature has, as a side effect, initiation of high-temperature polymerization reactions leading to development of polyaromatic hydrocarbons (PAH). PAH with number of rings larger than 3 makes up soot particles [5, 6] and, therefore, represent the most undesirable type of contaminants (tar). Tar is typically defined as polyaromatic hydrocarbons (PAHs) with molecular weights greater than benzene [7]. A producer gas contamination with tars can cause fouling in downstream equipment, leading to frequent shutdowns of the plant that significantly worsen its economic indicators. The best way to mitigate this problem is to find a feasible way to prevent PAHs origination and/or crack the PAHs into considerably lighter hydrocarbons, hydrogen, and carbon monoxide.

It is generally accepted that mixing of plasma and pyrolysis/gasification producer gas, facilitates decomposition of heavy hydrocarbons and tar into syngas. A complete mechanism of this decomposition is still unknown, but many researchers have come to the conclusion that free oxygen containing radicals, such as OH· radicals, are the most active radicals taking part in the breakdown reactions [8, 9]. It is widely felt that reactivity of a plasma gas is strongly dependent on the type of gas. An improvement in efficiency of thermal plasma gas utilization in decomposition of heavy hydrocarbons and tars is associated with a shift from using air and inert gases like N_2 and Ar as a working fluid of plasma torches to steam or to the mix of steam with other gases [10-14].

Combustion and, especially, acetylene/oxygen and hydrogen/oxygen combustions are associated with the highest adiabatic flame temperatures (calculated values of 3137^{0}C and 2807^{0}C, respectively [15]) which promote an origination of free radicals and their prolonged life time in the mix of combustion products. To some degree the flame (combustion gases at its highest temperature) could be considered as a plasma gas. In our previous publication [16], we reported that treatment of the reaction mixture containing the tar model compound toluene promoted its decomposition and the ratio CO/H_2 in syngas substantially depended on the flame employed.

The process, where hydrogen and oxygen have been produced via electrolysis of water followed by hydrogen/oxygen combustion could be also considered a way to generate plasma-steam by exploiting electricity. It has been reported [10, 11], that thermal efficiency of steam production in a plasma torch is in the range *51–70%* for an average temperature of the plasma jet at the torch outlet nozzle in the range of 2600K – 3500K. The efficiency of hydrogen and oxygen production for the entire electrolysis system is approximately 62% (the electrolyzer alone exhibits about 10% higher efficiency) [17]. As it follows from these data, the energy efficiency indicators for both systems are nearly the same.

However, a hydrogen burner seems more flexible, allowing different ratios between input hydrogen and oxygen flows and various options for heat utilization.

Hydrogen flame testing has been done for the reaction mixture consisting of the tar model compound toluene, steam, and nitrogen. Toluene has been selected as a tar model compound because it has been found in significant amounts in the products of biomass gasification [18], it has two functional groups, namely aromatic (phenyl), and aliphatic (methyl), and it is often used by many researchers to determine catalytic activity of different materials in tar destruction and decomposition [19-24]. The ability of hydrogen flame to convert toluene into syngas has been tested at the condition with no hydrogen content in the inlet reaction mixture; a presence of hydrogen in the feedstock usually decreases activation energy and facilitates that conversion [19, 20].

Thermodynamic calculations [25] show that at steam/carbon molar ratio 2:1 and larger and at the temperature 550^{0}C and higher, taking into account that the most possible apparent final products are benzene C_6H_6 (benzene), CH_4, H_2, CO, CO_2 [26], the conversion of toluene into benzene is negligible and mostly advances towards production of the last four components. The difficulty with which toluene decomposition proceeds is related to kinetic limitations, i.e. the presence of an activation energy barrier that either must be overcome (e.g., by a temperature increase) or decreased (e.g., by the introduction of active species or catalyst).

2 EXPERIMENTAL

2.1 The experimental setup

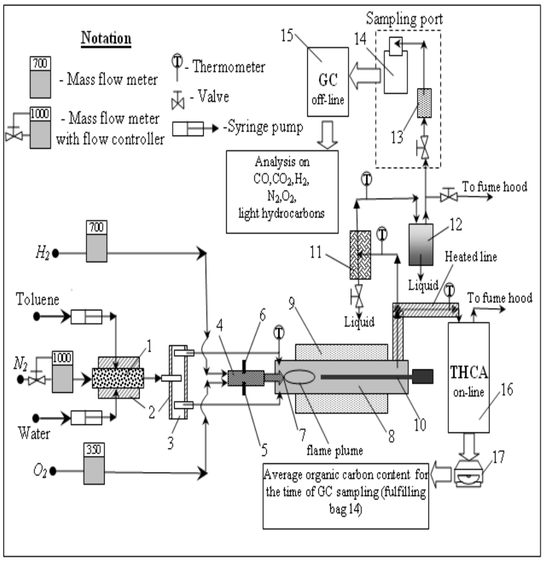

Figure 1: The experimental set-up. 1– evaporator (tube fulfilled with glass pebbles); 2 – heating tape; 3 – heated buffer (mitigates fluctuations in the vapor flows); 4 – torch handle; 5 – hydrogen valve; 6 – oxygen valve; 7 – torch tip; 8 – reactor; 9 – tube furnace; 10 – moving type K-thermocouple; 11 – condenser; 12 – demister; 13 – moisture trap; 14 – sampling Tedlar® bag; 15 – off-line gas chromatograph Agilent 7890A, 16 – on-line total hydrocarbon analyzer (THCA) 3000HM (Signal Instrument Company), 17–data recorder (Data Bridge™)

The effect of the treating of the mix of toluene, steam, and nitrogen with the hydrogen flame has been studied in the experimental setup presented in Fig.1.

Toluene and water are delivered into evaporator 1 by two separate syringe pumps NE-1000 (New Era Pump System Inc., Wantagh, NY, USA). The heat supply to evaporate liquid toluene and water is provided by heating tape 2 wrapped around evaporator 1. After evaporator 1, the blend of toluene, steam and nitrogen are directed into the heated buffer 3 which mitigates fluctuations in the flow rates of toluene and water vapors produced as a result of naturally unsteady evaporation process. Then this mix is supplied into reactor 8 which is housed inside tube furnace 9. The temperature of this blend at the reactor inlet is maintained in the range of 160-170^{0}C. The reactor is made of 316 Stainless steel tubing; it has a length of 76 cm and an inner diameter 2.1 cm. The burner consists of the torch handle 4 with fuel and oxygen needle valves 5, 6 and tip 7. They are taken from the torch kit 23-1003B manufactured by Smith equipment [27]. The torch tips have been customized (extended) in order to be inserted into reactor 8. The temperature in the reactor 8 is measured by moving a K-thermocouple 10 which provides temperature values that indicate whether or not the flame is extinct within the reactor 8. The flow of the produced gases downstream to reactor 8 is split into two streams.

The first stream is cooled in the condenser 11 and after liquids elimination in condenser 11 and demister 12, the flow goes to the fume hood or to the sampling port.

The sampling port consists of silica-gel moisture trap 13, and Tedlar® sampling bag 14. After gas collecting in a Tedlar® bag it is analyzed by Gas Chromatograph (GC) Agilent 7890A adjusted and calibrated for measuring refinery gas composition.

The second flow is directed to Total Hydrocarbon Analyzer (THCA) 16 and retained hot to keep all liquids in the gas phase. The temperature at the inlet of THCA is maintained in the range 170-190^{0}C. The flame ionization detector (FID) of the THCA detects the concentration of organic carbon in the gaseous flow, which means that its signal is linearly proportional to the concentration of all organic molecules multiplied by the amount of carbon in each. This proportion is valid (with slight deviations) for the mix of different hydrocarbons and aromatics [28] and has been successfully employed to measure tar in gasification products [29]. Every second a concentration of total organic carbon is recorded by a Data Recorder 17 and for the time of sampling gas into Bag 14 (about two minutes) the Data Recorder creates a file with the dynamic data. The average value of organic carbon content calculated from the data in this file is then analyzed together with the results of the gas analysis performed by an offline GC.

All gases are extra high purity (99.999%). Distilled water and toluene from Sigma-Aldrich with 99.8% purity have been used.

2.2 Experimental conditions

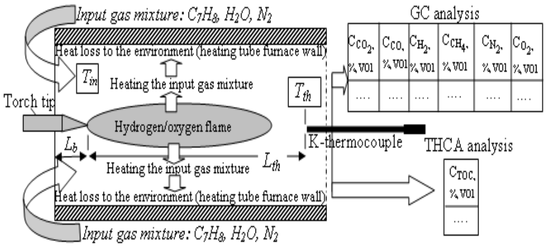

Figure 2: A process diagram for the flame interaction with the model reaction mixture in the reactor. L_b=1.5cm is the depth at which the torch tip has been placed into tube furnace, L_{th}=11cm is the distance between the torch tip and the type K-thermocouple, T_{th} is the temperature measured at that distance, T_{in}=160-170^{0}C is the temperature of the reaction mixture at the reactor inlet.

A flow diagram for the process of the reaction mixture interaction with hydrogen flame is presented in Fig. 2. The temperature at the reactor inlet (T_{in}) is maintained in the range 160-170^{0}C. The torch tip is inserted into the tube furnace at the depth of L_b=1.5cm. As it has been shown on flame profiles [30] a distance of about 10cm and larger from the tip of the burner is sufficient for the reaction between hydrogen and oxygen to be complete. On this basis, the distance between thermocouple and torch tip L_{th} has been taken equal to 11cm.

The basic experimental parameters of the input flows are presented in Table I.

Table I: Basic experimental parameters of the input flows

Hydrogen burner	
G_{O_2}, ml/min	350
G_{H_2}, ml/min	700
Reaction mixture	
L_{H_2O} (liquid), ml/min	0.27
$L_{C_7H_8}$ (liquid), ml/min	0.075
Steam/Carbon molar ratio	3:1
G_{N_2}, ml/min	1000
T_{in}, ^{0}C	160-170

For the experiment with no toluene ($L_{C_7H_8}$=0) in the reaction mixture, the concentrations of oxygen and hydrogen in the outlet gas flow lower than 0.5 vol% confirms a complete hydrogen/oxygen consumption as a result of stoichiometric combustion.

Seven tube furnace heating regimes are utilized in experiments. When the tube furnace is the only heat supplier to the reactor and reaction mixture (i.e. hydrogen burner is off), the temperature profiles of the gas flow within the reactor have a maximum $T_{\max}^{(k)}$ in the middle of the furnace. The temperature profiles for the heating regimes 1, 2, and 7 are presented in Fig. 3. The intermediate temperature profiles 3 to 6 are not shown here simply for maintaining clarity of the graph. In order to account for the steam produced by the hydrogen burner, temperature profiles have been measured for the water flow into evaporator L_{H_2O} = 0.8 ml/min.

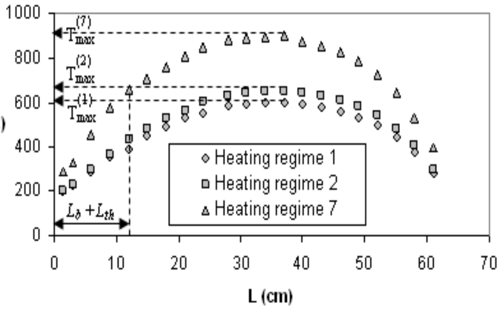

Figure 3. Temperature profiles of the gas in the reactor housed in tube furnace for different heating regimes. L is the current distance from the tube furnace inlet. $T_{\max}^{(k)}$ is the maximum temperature in the furnace for the k^{th} heating regime. Temperature profiles are obtained for G_{N_2}=1000ml/min, L_{H_2O}=0.8ml/min, $L_{C_7H_8}$=0; G_{O_2}=0, G_{H_2}=0 (burner is off).

2.3 Chemistry of toluene decomposition and data analysis

A desirable mechanism of toluene decomposition could be described as its endothermic steam reforming with production of synthesis gas

$$C_7H_8 + 7H_2O \Rightarrow 7CO + 11H_2 \quad \Delta H_{298}=+\,874\text{kJ} \tag{1}$$

coupled with a fast water-gas shift reaction

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad \Delta H_{298}=-41\text{kJ} \tag{2}$$

and assisted with hydrogen burning with oxygen in the burner

$$H_2 + \tfrac{1}{2}\, O_2 \Rightarrow H_2O \quad \Delta H_{298}=-242\text{kJ} \tag{3}$$

where ΔH_{298} is enthalpy of a reaction at standard condition (P=1atm., T=298K).

As discussed in [26] and [31] thermal decomposition of toluene likely proceeds through an intermediate production and steam reforming of benzene and methane coupled with fast water-gas shift reaction (2) as follows

$$C_7H_8 + H_2O \Rightarrow C_6H_6 + CO + 2H_2 \tag{4}$$

$$C_7H_8 + H_2 \Rightarrow C_6H_6 + CH_4 \tag{5}$$

$$C_6H_6 + 6H_2O \Rightarrow 6CO + 12H_2 \tag{6}$$

$$CH_4 + H_2O \Rightarrow CO + 3H_2 \tag{7}$$

The concentrations in the outlet gas of CO_2, CO, H_2, CH_4, and N_2 after condensation of all liquids are measured by the GC. Maintaining the volumetric flow rate of N_2 constant G_{N_2}=1000ml/min during the experiment allows the flow rates of analyzed gases to be calculated as follows

$$G_i = (C_i\, G_{N_2})/C_{N_2} \tag{8}$$

where G_i and C_i are volumetric flow rates and concentrations of i-th component, respectively; i is CO_2, CO, H_2, CH_4.

In order to apply equation (8) to estimate the volumetric flow rate of total organic carbon, the average volumetric concentration C_{TOC}^{mes} measured by the THCA should be recalculated for dry conditions C_{TOC}^{dry} by using a transfer coefficient K as follows

$$C_{TOC}^{dry} = K C_{TOC}^{mes} \tag{9}$$

Taking into account that the input toluene concentration in N_2 is just 1.7 vol% and therefore the impact of the evolved hydrocarbons and aromatics on the total output gas flow at dry conditions is negligible, the transfer coefficient K is calculated as follows

$$K = (\textstyle\sum G_i + W_1 + W_2 - W_R)/\sum G_i \tag{10}$$

where $\sum G_i$ is the sum of volumetric gas flows of N_2 and CO_2, CO, H_2, CH_4 obtained by using formula (8); W_1 is the water steam flow formed as a result of hydrogen combustion in the burner, W_2 is the water steam flow formed as a result of water flow L_{H_2O} evaporation in evaporator 1 (Fig.1), W_R is the water steam flow consumed in reactions (1) and (2) to produce H_2. A calculation of W_R is based on stoichiometric ratios as follows

$$W_R = \left(7/11\frac{C_{CO}}{C_{CO_2}+C_{CO}} + 14/18\frac{C_{CO_2}}{C_{CO_2}+C_{CO}}\right) G_{H_2} \tag{11}$$

The volumetric total organic carbon flow rate is then calculated the same way as for all other gaseous components as follows

$$G_{TOC} = C_{TOC}^{dry}\, G_{N_2} / C_{N_2} \tag{12}$$

The input volumetric flow of toluene $G_{C_7H_8}^{in}$ fluctuates due to the unsteady nature of evaporation; therefore, its value is derived from the values of the output flows of carbon-containing species as follows

$$G_{C_7H_8}^{in} \approx \left(G_{CO_2} + G_{CO} + G_{CH_4} + \frac{G_{TOC} - G_{CH_4}}{R_f}\right)/7 \tag{13}$$

where R_f is a FID response factor of carbon atoms in aromatics relative to methane. It has been taken equal to 0.9, slightly lower than for methane [32].

2.4 Efficiency indicators

Consistent with the purpose of the hydrogen burner to facilitate toluene decomposition into syngas, the following efficiency indicators are introduced. Toluene conversion η_T into CO_2 and CO is determined as follows

$$\eta_T = \frac{G_{CO_2} + G_{CO}}{7 G_{C_7H_8}^{in}} \tag{14}$$

Syngas production efficiency is defined as the ratio of produced H_2 and CO to their maximum possible amount as follows

$$\eta_{sg} = \frac{G_{H_2} + G_{CO}}{18 G_{C_7H_8}^{in}} \tag{15}$$

For the case when there is an oxygen excess in the burner and, therefore, toluene steam reforming is combined with toluene partial oxidation, syngas production efficiency is defined as follows

$$\eta_{sg}^{ox} = \frac{G_{H_2} + G_{CO}}{18 G_{C_7H_8}^{in} - 1/2 \Delta G_{O_2}} \tag{16}$$

where $\Delta G_{O_2} = G_{O_2} - G_{O_2}^{st}$ is an excess of the oxygen volumetric flow G_{O_2} over its stoichiometric amount, $G_{O_2}^{st}$.

3 RESULTS AND DISCUSSION

3.1 Efficiency indicators as a function of temperature

Fig.4 presents a variation of toluene conversion and syngas production efficiencies, η_T and η_{sg}, with temperature T_{th} measured by the type K-thermocouple (Fig. 2) for the basic input parameters presented in Table I. A change in T_{th} proceeds towards a steady state condition in concert with all output concentrations. T_{th} is always higher than those maximum temperatures in the middle of the tube furnace when the burner is off (as seen for heating regimes 1 and 2 in Fig. 3). Therefore, the heat released by the hydrogen burner is absorbed both by the reaction mixture and tube furnace walls. The heat absorbed by the tube furnace is associated with the heat losses, hence, switching heating regimes from 1 to 2 helps to reduce those losses. A similar effect should be associated with an increase in the temperature of the inlet reaction mixture T_{in}.

The heat supplied by the hydrogen burner is also utilized to perform endothermic toluene conversion into syngas (reaction (1)). Toluene conversion η_T and syngas production η_{sg} increase with increasing T_{th} and reach values of about 85%. The inequity $\eta_T > \eta_{sg}$ is present for all experimental data; this imbalance could be explained by a presence of some products in the output gas flow whose C to H ratio is lower than in the introduced toluene (e.g., methane).

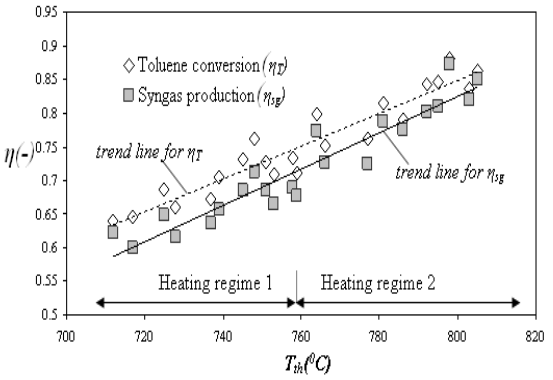

Figure 4: Variation of toluene conversion and syngas production efficiencies with the thermocouple temperature T_{th}. During experiments this temperature rises with time approaching steady state conditions corresponding to tube furnace heating regime 1 or 2 (Fig.3). All input flow parameters are basic (Table I).

Fig. 5 presents calculated liquid toluene flow $L^{calc}_{C_7H_8}$ for the same points as in Fig.4. The values are calculated through $G^{in}_{C_7H_8}$ (equation (13)) followed by their conversion to mass flow rate and then by using density of liquid toluene to $L^{calc}_{C_7H_8}$. A comparison with the supplied toluene flow rate $L_{C_7H_8}$ (Table I) shows, that as a result of the unsteady nature of evaporation, the calculated rate $L^{calc}_{C_7H_8}$ fluctuates about the supplied rate with a maximum deviation of roughly 25%. Fluctuating input gaseous flows of toluene affects directly (linearly) denominators of efficiency indicators (equations 14-16) and indirectly (not linearly) but in the same direction their numerators as a response to that change. A significant excess of steam allows its fluctuations to be regarded as a minor factor. Due to the statistical nature of the fluctuations in gaseous toluene flow, the experimental results are considered as a trend in response to a change in other than toluene flow rate experimental conditions. For instance, as seen in Fig. 4 an increase in the temperature of the gas in vicinity of the type K-thermocouple explicitly leads to increasing toluene conversion η_T and syngas production η_{sg} efficiencies.

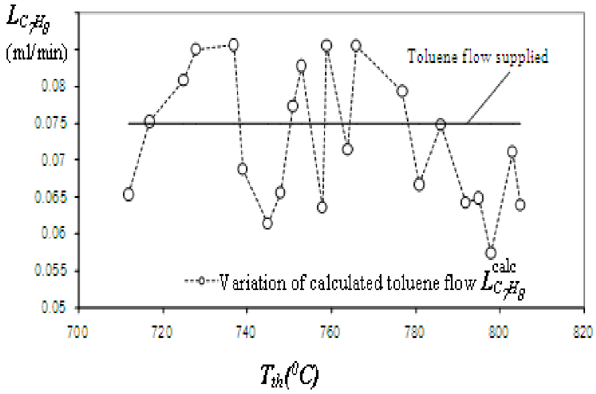

Figure 5: Variation of calculated toluene flow $L_{C_7H_8}$ for the same experimental points as presented in Fig.4.

3.2 Combination of toluene steam reforming with partial oxidation (hydrogen combustion in excess of oxygen in the burner)

Application of a hydrogen flame to treat gasification/pyrolysis producer gas implies degradation in the quality of energy, i.e. conversion of hydrogen heating value (especially if generated by using electricity) into sensible heat of the gas. However, it should be noted that the same heating value of the producer gas is recovered meaning that "external" hydrogen is burnt instead of the producer gas. Accounting for energy efficiency indicators for a gasification process, hydrogen burner utilization should be limited and combined with the regularly employed air/oxygen introduction into the mix of organic gases in order to increase their temperature and crack or decompose them into syngas.

In our experimental setup an extra amount of oxygen has been introduced through the hydrogen burner by means of increasing oxygen flow into it. The maximal addition to the stoichiometric flow of oxygen (Table I) $\Delta G^{\max}_{O_2}$ = 60 ml/min is calculated according to the following partial oxidation reaction

$$C_7H_8 + 3.5O_2 = 7CO + 4H_2 \quad \Delta H_{298}=-724kJ \qquad (18)$$

The value of ΔG_{O_2} has been varied from 0 to 60 ml/min, which corresponds to a change in the toluene equivalence ratio φ from 0 to 0.4. The equivalence ratio φ is defined as the ratio between supplied oxygen and the oxygen needed for stoichiometrically complete combustion of toluene.

The theoretical maximum of syngas production through reactions (1) and (2) is reduced as a result of oxygen introduction and consequential combustion of some part of H_2 and CO. This is accounted for in the modified efficiency indicator η_{sg}^{ox} (17).

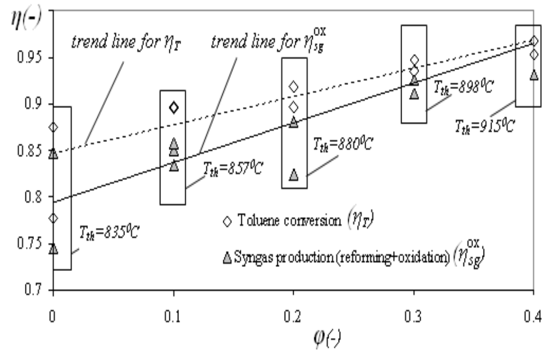

Figure 6: A dependence of toluene conversion η_T and syngas production η_{sg} efficiencies on equivalence ratio φ for toluene. Rectangles emphasize measurements taken at the same φ and thermocouple temperature T_{th}. Tube furnace heating regime is 2 (Fig.3), all other parameters except oxygen flow into the burner G_{O_2} (see text) are basic (Table I).

As presented in Fig. 6, with increasing toluene equivalence ratio φ, toluene conversion efficiency η_T and syngas production efficiency η_{sg}^{ox} increase and reach values higher than 90%. As expected and as seen in Fig. 7, with increasing excess oxygen the syngas quantity decreases (mostly due to a decrease in H_2 content).

However, syngas production efficiency η_{sg}^{ox} for the case considered approaches its maximum values (Fig. 6).

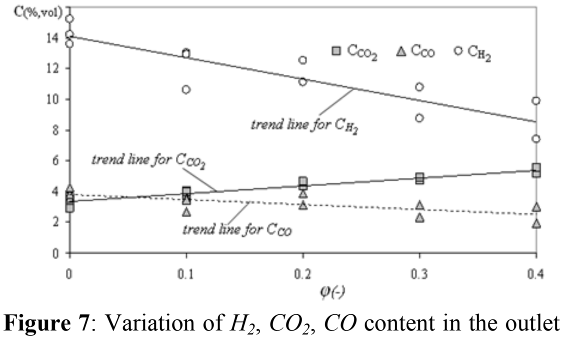

Figure 7: Variation of H_2, CO_2, CO content in the outlet gas flow with equivalence ratio φ for toluene. Tube furnace heating regime is 2 (Fig.3), all other parameters except oxygen flow into the burner G_{O_2}(see text) are basic (Table I).

3.4 Steam reforming and partial oxidation of toluene when hydrogen burner is off

As seen in Fig. 8, in the absence of the hydrogen burner toluene conversion increases with temperature, however it is characterized by significantly lower efficiency indicators when compared to Fig. 4. It is worthwhile to note that when the burner is off, the heat supply to the reaction mixture comes only from the tube furnace and in order to obtain temperature dependence (Fig.8) heating regimes are switched i.e the regime with T_{max} around 700⁰C (heating regime 3) is switched to the regime with T_{max} about 750⁰C (regime 4), and then to 800⁰C (regime 5), 850⁰C (regime 6), and 900⁰C (regime 7) (Fig. 3).

When the burner is on, the reaction mixture is heated as a result of hydrogen combustion and the tube furnace is acting as a heat absorber (Fig. 2).

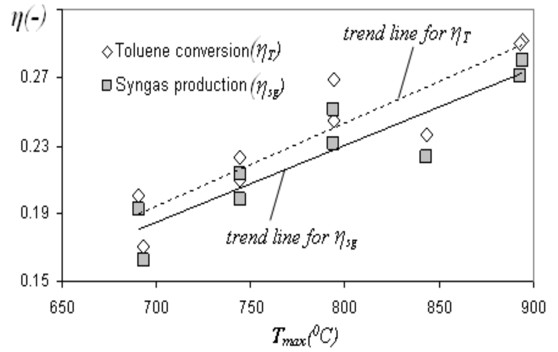

Figure 8: A dependence of toluene conversion η_T and syngas production η_{sg} efficiencies on maximum temperature (T_{max}) in the middle of the furnace. T_{max} is associated with different heating regimes in tube furnace. Hydrogen burner is off (G_{O_2}= G_{H_2}=0). Water flow rate L_{H_2O}=0.8ml/min accounts for the steam produced by hydrogen burner, all other parameters are basic (Table I).

As presented in Fig. 9, a combination of steam reforming with partial oxidation leads to a certain increase in efficiency of toluene conversion η_T .

However, with increasing oxygen input (ΔG_{O_2} and φ) syngas production efficiency η_{sg}^{ox} passes through a maximum and then drops substantially, following hydrogen concentration in the outlet gas flow (Fig. 10).

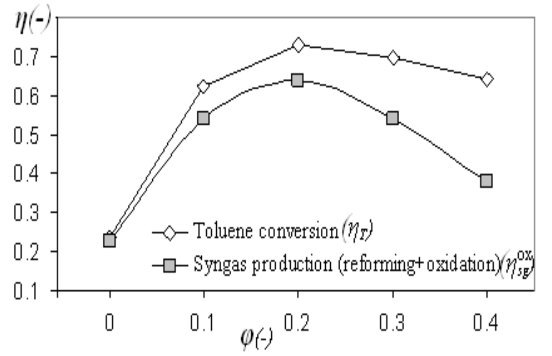

Figure 9: Dependence of toluene conversion η_T and syngas production η_{sg} efficiencies on equivalence ratio φ for toluene. Hydrogen burner is off (G_{H_2}=0), however, G_{O_2}=Δ G_{O_2} is changing from 0 to 60 ml/min. T_{max} in the middle of furnace varies insignificantly and stays in the range 840-850⁰C. Water flow rate L_{H_2O}=0.8ml/min accounts for the steam produced by hydrogen burner, all other parameters are basic (Table I).

When the hydrogen burner is on, the efficiency of syngas production η_{sg}^{ox} constantly increases (Fig.6) because a decrease in hydrogen concentration (Fig. 7) is slow and partially offset by a greater toluene conversion into syngas.

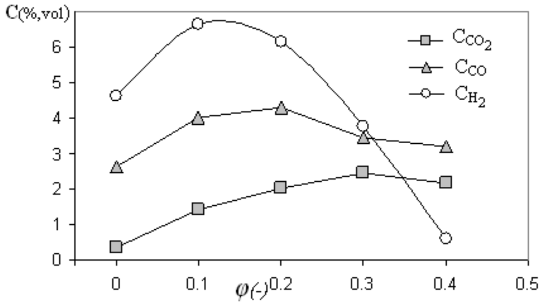

Figure 10: Variation of CO_2, CO, H_2 contents in the outlet gas flow with equivalence ratio φ for toluene. All parameters are the same as in Fig. 9.

3.5 Implication of experimental results to a mechanism of toluene (tar) decomposition

A presence of oxygen and steam in the reaction mixture with toluene could induce two reaction pathways: steam reforming and oxidation (Fig.11). As it is generally accepted, both of them proceed through intermediate activated complexes whose origination is greatly promoted by elevated temperatures and mixing with active chemical species (radicals). Radicals especially OH· radicals tend to abstract a hydrogen atom from an organic molecule. The organic molecule gets excited and starts to participate in decomposition, oxidation, and other reactions. As follows from Figs. 9 and 10 with hydrogen burner is off, an increase in oxygen content in the reaction mixture leads to suppression of the steam reforming reaction path. This is reflected by an increasing gap between toluene conversion η_T and syngas production η_{sg}^{ox} efficiencies. This could be partially explained by the fact that the rate of hydrogen oxidation is an order of magnitude greater than that of CO and various organics [33,34].Therefore, with rising oxygen content hydrogen consumption increases rapidly through combustion and its participation in saturation of double bonds to alleviate steam reforming and prevent polymerization reactions [35] becomes very limited.

When the hydrogen burner is on, steam reforming is considerably accelerated so that oxidation follows syngas generation (Fig.11) and, therefore, syngas production efficiency η_{sg}^{ox} increases in concert with toluene decomposition η_T (Fig.6). This fact is of great importance for an optimal combination of external (hydrogen burner) and internal (partial oxidation) heat supply to pyrolysis/gasification products.

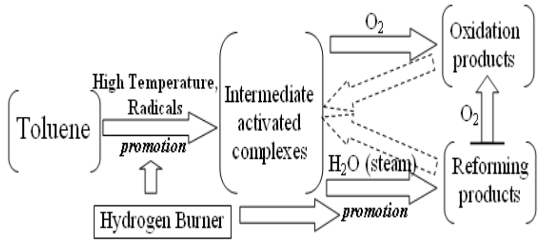

Figure 11: Hydrogen burner influence on a toluene (tar) decomposition mechanism

4 CONCLUSION

The conducted experiments clearly indicate that treatment of toluene (a model tar compound) blended with steam and nitrogen (reaction mixture) with the oxy/hydrogen flame promotes toluene steam reforming into H_2 and CO. Steam reforming of condensed (low hydrogen content) organic molecules is associated with a rigorous decomposition of water along with destruction of organic molecules.

A certain excess of oxygen in the flame promotes almost complete toluene decomposition into syngas in the regime of its partial oxidation. In spite of some reduction in the total volume of syngas produced, the excess of oxygen in the hydrogen/oxygen flame could be efficiently applied to the syngas contaminated with tars; this allows the original syngas heating value to remain unchanged.

In general, a hydrogen flame could be applied to convert different types of volatile organic compounds and tars into syngas, however, in order to be energy efficient an optimal combination between external (hydrogen burner) and internal (partial oxidation) heat supply is required. The use of a hydrogen flame seems quite competitive to thermal plasma gas for utilization in gasification technologies, meaning that hydrogen and oxygen can be produced by electrolysis of water (or supplied separately). The efficiency of electricity utilization to make the hydrogen/oxygen flame in order to decompose volatile organic compounds and tars will be the subject of upcoming studies.

5 NOMENCLATURE

C	concentration, %vol
FID	flame ionization detector
G	gas flow rate, ml/min
GC	gas chromatograph
H_{298}	enthalpy at standard conditions
K	transfer coefficient
L	liquids flow rate, ml/min
L	distance, cm
P	pressure, atm
PAH	polyaromatic hydrocarbons
R_f	response factor
T	temperature ^{0}C or K
THCA	total hydrocarbon analyzer
W	water steam flow rate, ml/min

Greek symbols

φ	equivalence ratio

η_T	toluene conversion efficiency
η_{sg}	syngas production efficiency in steam reforming
η_{sg}^{ox}	syngas production efficiency in steam reforming combined with partial oxidation
Δ	difference

Subscripts

b	burner
i, x, y	indexes
in	input
max	maximum
R	reaction
TOC	total organic carbon
th	thermocouple

Superscripts

calc	calculated
dry	dry condition
in	input
k	k-th heating regime
mes	measured
st	stoichiometric

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