**Pyrolytic toluene conversion to benzene and coke over activated carbon in a fixed-bed reactor**

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**Abstract**

The catalytic decomposition of tar compounds is an important issue in the cleaning and upgrading of gasification product gases. This work focuses on toluene pyrolysis in a quartz tube reactor with a fixed bed of activated carbon. A toluene to benzene and coke conversion mechanism is also proposed. Liquid decomposition products were analysed with GC-FID. The ash content in the spent carbon was measured, allowing for the determination of coke deposit growth on the carbon surface. Pyrolysis runs were performed at temperatures ranging from 650 – 800 °C and with varying toluene feeding times. It was determined that toluene conversion is maintained above 90% for the first 20 min of pyrolysis at 800 °C. At this initial time, pronounced coking on the carbon surface was observed. Subsequently, toluene conversion decreased, coke deposition was hindered and benzene, a decomposition side product, yield was greatly enhanced. At lower temperatures coking is inhibited and toluene conversions were relatively low. For short, 10 min feeding time and at low temperatures, benzene share in overall converted toluene is significant. The toluene to benzene conversion model, necessarily based on both experimental results and the literature, shows that coke and benzene creation are competing reactions.

**Keywords:** activated carbon, pyrolysis, coke

# 1. Introduction

Biomass gasification is an important and rapidly developing renewable energy technology. One major obstacle is the substantial tar yield from the process. Produced tar causes clogging of pipelines of an installation and prevents the direct use of a producer gas in gas engine or turbines. Tar can also contribute to the diminished calorific value of a syngas. Therefore various methods for tar cracking are being extensively studied to improve gasification performance [1, 2]. Since the overall tar conversion process comprises a vast variety of thermochemical conversion pathways, decomposition of selected tar compounds is often studied experimentally [3, 4].

Toluene as a model tar compound has been previously studied [3, 5-7], although conversion over catalyst beds was usually performed in a slightly oxidative atmosphere (usually with steam) where reforming reactions of toluene and toluene derived coke might take place. Bhandari et al. [5] studied toluene pyrolysis over activated carbon and biochar in pure N2 at 700 and 800 °C. Catalyst deactivation with time-on-stream was observed, as well as the creation of some gaseous products, such as CO2, CO, H2 and CH4. They also reported a 25% and 85% decrease of biochar and activated carbon surface area, respectively, after a 4 hour run.

Detailed toluene decomposition pathways were examined at higher temperatures and different pressures but with no catalyst present, e.g. in shock tubes [8-14]. The initial step of toluene conversion involves the formation of phenyl or benzyl radicals according to the reactions:

(1)

(2)

Reactions 1 and 2 are reported to occur without catalyst presence at temperatures above 1000 °C [11, 14], which are higher than reaction temperatures in the present work. Benzyl radicals are the main product of the decomposition and it was determined that they undergo further conversion to cyclopendadienyl radicals (c-C5H5) directly or through a fulvenallene intermediate (C7H6) [8, 11, 15, 16]. c-C5H5 can consecutively decompose to a propargyl radical (C3H3). Acetylene is released as a side product of c-C5H5 to C3H3 and direct benzyl to c-C5H5 decomposition [11]. In these conditions, benzene is reported to be created mainly by hydrogen attack on the toluene molecule [11]:

(3)

Other possible pathways are a termination reaction of phenyl and hydrogen radicals as well as the rearrangement of two propargyl radicals [11]:

(4)

(5)

Since most of the tar decomposition reactions have a radical mechanism, the presence of radical sources strongly affects hydrocarbon conversion. It was reported by Zimmerman and York [17], that in the excess of hydrogen, due to hydrogen dissociation, toluene demethylation to benzene can undergo with efficiency as high as 95%. Moreover, addition of heptane to the reaction environment enhanced dealkylation, probably by increasing the amount of free radicals in the gas phase [17].

Even without a catalyst present, some coke formation has been observed in high temperature experiments in shock tubes as well as in acetylene flames [9, 11, 18]. It is ascribed to the three most plausible mechanisms, namely: hydrogen abstraction – C2H2 addition (HACA) [19], cyclopentadienyl radical recombination (CPDR) and phenyl addition/cyclisation (PAC) [13]. PAHs and consequently soot formation through acetylene addition is the most common mechanism in acetylene flames at high temperatures [18]. During aromatic hydrocarbons conversion it might take place as well due to the C2H2 being created as a side-product [12]. However, the PAC mechanism was reported to be a dominant one in toluene/benzene pyrolysis, because of the observed increase in PAH molecules with increments of 74 mass units (resulting from phenyl addition, H atom elimination and cyclisation) as well as the rate of soot formation being too large to be ascribed solely to the HACA mechanism [13]. Cyclopentadienyl radical rearrangement is also believed to take place, during the later steps of PAHs growth [13].

Coke deposition on catalysts during hydrocarbon thermal processing, like cracking or alkylation, is a common issue in the chemical industry [20-26]. Aluminosilicate materials like zeolites are common catalysts in hydrocarbon chemistry, due to their well-defined pore structure and versatile acidity. Properties of the coke retained in zeolite pores are proved to be highly dependent on the reaction temperature and catalyst structure [21, 27-30]. Coking properties of different hydrocarbons were studied extensively over different zeolite types [27, 31, 32]. Generally, at lower temperatures (~150 °C) coke is comprised of derivatives of the hydrocarbon feedstock and is retained in the zeolite pores partially because of the large coke molecule sizes but mainly due to the low volatility of the coke compounds [27]. At higher temperatures (above 350 °C), the boiling point of coke species is lower than the reaction temperature, therefore compounds are retained within the zeolite mostly because their growth is fast enough for them to reach molecule sizes larger than the zeolite pores and therefore they become trapped within the zeolite structure [27, 28]. The initial hydrocarbon decomposition starts over acidic sites or metals on the surface of the catalyst. For acid catalysts, the coking process starts with hydrogen transfer, while for bifunctional catalysts it is initialised, most likely, through a dehydrogenation step on surface metals. Since activated carbons have both functional groups and AAEM species metals on their surfaces [3, 33-35], it is expected that either of the initialisation pathways can occur. Further reactions in the activated carbon pores involve condensation and rearrangement of the molecules. In reported experiments, the coking mechanism involves ion creation, such as in the case of toluene, where a benzenium ion is created [27, 28]. The tests performed in this study were carried out at much higher temperatures, therefore it is expected that toluene decomposition and coke creation are radical reactions [36].

The nature of the coke derived at temperatures higher than 350 °C is reported to be independent of the native feedstock molecule and highly correlated to zeolite pore structure and size. Coke molecule size increases with time-on-stream or retention time as a result of further rearrangement reactions [23, 27, 28]. Therefore, the coke derived from toluene pyrolysis at temperatures above 800 °C is expected to consist mainly of heavy particles insoluble in organic solvents with sizes and shapes corresponding to the activated carbon pores. Since activated carbon pore sizes are larger than that of zeolites [5, 21, 37-39], limitations of coke molecule growth in this case might be less significant.

Since most of the toluene pyrolysis experiments and models were performed non-catalytically at very high temperatures, or with a presence of a catalytic bed but at temperatures substantially lower than the ones in this study, it is difficult to unambiguously determine what mechanisms are governing the decomposition of toluene in this research. Therefore, some most probable scenarios can only be assumed.

This work focuses on toluene decomposition pathways over an activated carbon bed. Moderate temperatures are used in the range of 600 – 800 °C. Time-on-stream impact on carbon deactivation, coke deposition and benzene creation are also examined. All runs are performed in an inert nitrogen atmosphere. A toluene to benzene and coke conversion mechanism is also proposed.

# 2. Experimental

Experiments with toluene conversion over activated carbon (AC) were performed in a laboratory quartz tube reactor. Different feeding times and temperatures were applied to study the performance of AC in an inert atmosphere, were no steam or CO2 reforming occurs. Unreacted toluene, as well as any liquid conversion products, were analysed by GC-FID. The ash content in spent AC samples was analysed allowing for the detection of any toluene that may have coked on the carbon surface.

# 2.1. Materials

The catalytic material utilised in this work was a commercial activated carbon AC with particle sizes in a ranging from 0.4 – 0.85 mm and a surface area of 1000 – 1100 m2/g. Elemental and ash compositions are reported in Tables 1 and 2, respectively.

As a representative of tar compounds, 99.5% toluene from POCH S.A (Avantor Performance Materials) was used. For GC calibration purposes, 99.8% ethylbenzene from Chempur and 99.5% benzene from POCH S.A. were obtained. GC calibration standards as well as toluene trapping were performed in 99.5% dichloromethane from POCH S.A.

Gases used in the experiment were as follows: 5.0 purity air with a hydrocarbon content below 0.1 ppm, 5.0 N2 and 6.0 He from Air Liqude. 5.0 purity H2 for FID was produced *in situ* with a SPE150HC hydrogen generator.

Table 1. Activated carbon ultimate analysis and ash content in wt. % on a dry basis, O by diff

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| C | H | N | S | O | ASH |
| 81.45 | 0.43 | 0.53 | 0.66 | 2.53 | 14.4 |

Table 2. AC ash composition in wt. % on a dry basis

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| SiO2 | 65.70 |  | SO3 | 0.18 |
| Fe2O3 | 2.49 |  | P2O5 | 1.47 |
| Al2O3 | 24.90 |  | Na2O | 0.42 |
| Mn3O4 | 0.02 |  | K2O | 0.77 |
| TiO2 | 0.72 |  | BaO | 0.08 |
| CaO | 2.31 |  | SrO | 0.13 |
| MgO | 0.29 |  |  |  |

# 2.2. Experimental apparatus

As presented in Fig. 1, the main element of the test rig is a quartz tube reactor (1) enclosed in an electrical two-zone furnace (2). Each zone has a separate control panel (3) allowing for different operating temperatures within two reactor zones. Moreover, furnace fastenings enable the movement of the two sections along the reactor axis, such that the unheated space between two zones can be adjusted. In this work, the upper zone serves as an evaporator for the dosed compound, while the conversion on a fixed bed takes place in the lower heating zone. Space between the sections is insulated with ceramic fittings. The quartz tube inner diameter is 20 mm, while the upper and lower heating zones are 200 and 300 mm high, respectively.

The quartz reactor is connected to piping with gas tight KF flanges. To the upper end of the reactor, N2 flow from a gas cylinder is supplied. Toluene is constantly fed to the reactor by means of a syringe pump (4) equipped with Agilent microsyringe connected with tubing that ends with a needle that is inserted into the reactor. To accommodate the needle, a hole in the quartz tube wall was drilled above the first heating section and was later sealed with high temperature silicone. As a result, a septum was created allowing for gas tight needle injections into the reactor. In the upper section of the reactor, quartz wool is placed so that a dosed compound can evaporate from the wool surface. Below, in the second section, a catalyst bed can be placed supported by a quartz wool layer. The reactor is connected by Teflon tubing to the sampling train (5) where the unreacted compounds as well as any conversion products are trapped. The trap consists of impinger bottles with G-3 frits filled with 50 mL of dichloromethane and kept in a cold bath at ca. -25 °C.

Bed temperature is constantly measured by an N type (NiCrSi-NiSi) thermocouple (6) inserted through the bottom of the reactor in a protective quartz tube with an outer diameter of 3 mm.

As shown in Fig. 2, the temperature profile in the lower zone was measured to establish where the sample should be placed. The height of the uniform-temperature zone is particularly important when the furnace is used to produce char from a raw biomass, since it determines maximum bed height of the feedstock.



Fig. 1. Test rig diagram 1 – quartz tube reactor, 2 – two-zone furnace, 3 – controller panels for furnace sections, 4 – syringe pump, 5 – cooled trap, 6 – thermocouple with a display

Utilised region with uniform heating profile

Fig. 2. Ratio of an actual furnace temperature to the set temperature with respect to the height of the lower zone of the furnace

# 2.3. Experimental run procedure

In order to perform the toluene decomposition on activated carbon bed, the following procedure on the test rig described in section 2.2. was developed.

To avoid oxidation, activated carbon samples were stored in a desiccator under a reduced-oxygen atmosphere. The quartz tube was packed with 1 g of a sample, placed between quartz wool supporting layers (approx. 0.4 g) at the middle of the lower heating zone. The height of AC bed was approximately 8 mm. In the part of the tube enclosed in the evaporator, another layer of quartz wool was placed as a support for evaporating toluene. To remove oxygen from the system, the reactor was purged with N2 for 10 min after which the heating of both furnace zones started. The upper zone was heated up to 200 °C and the lower zone was kept at an operating temperature range of 650 – 850 °C, depending on the run. The impinger bottle with a G-3 frit and 50 mL of dichloromethane was cooled in a -25 °C bath. Preliminary studies showed that toluene recovery in the first bottle was above 95% and that there were negligible amounts of toluene captured in the consecutive bottles. Therefore, in all the operational runs, a single impinger was used. After reaching operating temperatures, the impinger bottle was connected to the reactor. The whole system was purged with N2 for 15 min to stabilise temperature in the impinger. Thereafter, toluene feeding began. Feeding velocity was set to a constant value resulting in the toluene-in-N2 concentration of 8 g/Nm3. Compound dosing was varied by changing the feeding time in a range of 5 – 50 min. After the dosing was finished, the reactor and impinger were purged for a further 15 min to remove all the toluene vapour from the reactor. Finally, the impinger was disconnected from the line and its content was analysed with GC while the AC was cooled down in the N2 flow to an ambient temperature, and was thereafter stored in a desiccator under the O2-depleted conditions.

Before the main test runs were performed, blank tests were conducted, namely: toluene recovery in an empty reactor and a run with only quartz wool layers, both at 800 °C. The rig was monitored to determine if any liquid products of AC decomposition were formed after heating to 800 °C for an hour. It was established that no thermal cracking of the toluene in an empty reactor or on the quartz wool surface took place. No dichloromethane-soluble products of AC annealing were detected. During all the runs, no coke deposition was observed above the AC bed. There were however, small, negligible amounts of deposit gathering on the quartz tube walls below the bed.

# 2.4. Impinger content and spent char analysis

Ethylbenzene was utilised as internal standard and was added to all dichloromethane solutions collected from the impingers. Absorbed compounds were analysed with an Agilent 6890N GC-FID chromatograph equipped with an Agilent 7893 autosampler. A HP-5 30 m capillary column and He as a carrier, were used for all the analyses. Since no heavier compounds were detected in the solution, the heating rate at the higher temperature range was increased and the GC method was set as follows: initial temperature was set to 50 °C and was maintained for 5 min. The temperature was raised to 80 °C at a rate of 5 K/min. The heating rate was then increased to 10 K/min to a final temperature of 200 °C where it was held for 2 min. The inlet and detector were kept at 250 °C and a 1 μl injection was made with a split ratio of 10:1.

Since no detectable amounts of ethylbenzene were observed in the solutions before the addition of a standard and the analyte/standard response factor was constant within the measured concentrations, it was decided to use internal standard calibration method. Toluene and benzene concentrations were also determined from the calibration curves and were found to be in agreement with internal standard results for most of the runs. The decision to use an internal standard method was based on the observation that sometimes the response of the detector is slightly increased and the calibration curve method would provide inaccurate data whereas the response factor for the analyte/standard remains the same. This phenomenon could be due to the flow rate variations of the carrier gas in the GC [40].

Coke deposition on chars from the experimental runs was determined by analysis of the ash content in the spent char samples. Analysis was performed in a muffle furnace at 815 °C. First a Al2O3 dish was heated at 815 °C for 60 min, cooled down in a desiccator and weighted. Next the 0.7 g of spent char sample (dried at 105 °C for 2 h) was placed inside the dish. The sample was heated at 815 °C for 2 hours then cooled down in a desiccator and subsequently weighted. The ash content was calculated based on the mass loss. Coking behaviour characteristic was therefore obtained, since as the amount of coke deposit increases, the ash content in the spent char decreases. Most measurements were made in duplicate. Some inconsistency in the results may have been caused by a non-uniform structure of AC ash (Fig. 3) or a presence of powder from the quartz wool in the char sample.



Fig. 3. Non-uniform reddish discoloration visible in the ash derived from spent char combustion

# 3. Results and discussion

The conversion of toluene, shown in Fig. 4, was calculated as

(6)

where is the mass of toluene fed to the reactor and is the mass of toluene recovered in an impinger bottle. For the first 20 minutes the conversion remained above 90%. This period corresponds to a 0.095 toluene-to-AC mass ratio. After this point, the conversion constantly decreased to reach approx. 65% after 50 min. All runs showed in Fig. 4 were conducted at 800 °C. It was, however, observed that temperature has a very significant impact on toluene conversion (Fig. 5). With the conversion as low as 16% at 650 °C, there is an exponential growth up to above 90% at 800 °C, after which the conversion levels off. During these runs, the same toluene-to-AC mass ratio of 0.048 was maintained which corresponds to a 10 min feeding time.

In Fig. 6 and Fig. 7 the ash content in spent AC samples is shown for constant temperature and constant feeding time runs, respectively. In both cases, a decreasing trend can be observed, especially at the lower temperature/feeding time values. The ash content depletion corresponds to a higher fixed carbon share in the AC which is most likely a result of coke formation from toluene thermal decomposition. The highest increase of coke deposition takes place within the first 20 min of toluene feeding, while at the same time, the AC activity remains constant at above 90%.

The increase of coking with temperature (Fig. 7) suggests that the coke deposition reaction occurs at higher temperatures. Poor toluene conversion at lower temperatures (650-700 °C) is therefore not influenced by AC deactivation by coke deposition and most likely can be assigned strictly to a temperature effect.

A high toluene conversion at 800 °C is maintained for the first 20 min of the feeding, when the activated carbon is still active. During this time, coke, as one of the conversion products, is continuously depositing on the AC surface, hindering its active sites and causing deactivation [2, 41]. Catalyst poisoning by carbon residue is a phenomenon well known in hydrocarbon thermal treatment processes, especially under a reducing atmosphere [3, 24, 42]. As can be seen in Fig. 6, after the initial 20 min, the coking process is suppressed, most likely due to AC surface saturation with coke deposits. Toluene conversion still proceeds but it is greatly inhibited. As the overall conversion for longer feeding time runs decreases linearly (Fig. 4), approximately only half of the toluene that was fed to the reactor after the initial 20 min is converted. However, it must be emphasised that even with the coke-covered AC, some toluene is still decomposed, either due to the radical chain reactions that were initialised by the fresh AC or most likely because the coke surface is still able to interact, although to lesser extent, with toluene particles.

In lower temperatures (Fig. 7), coking reactions are slower or do not occur at all. Despite the lack of AC deactivation, toluene conversion is low because of the temperature influence on reactions rates (Fig. 5). Therefore, to maintain catalyst activity in commercial installations, it is important to maintain sufficiently high temperatures while introducing some oxidising compounds (steam, CO2) to allow for the continuous decomposition of depositing coke [43, 44].

The only liquid product of toluene conversion that was found in the impinger bottle was benzene (Fig. 8 and Fig. 9). The yield of benzene was expressed in two ways. First, based on the amount of toluene fed to the reactor and second by the amount of toluene that was converted during the run. The benzene/toluene mass ratios were therefore calculated as follows:

(7)

(8)

where is the mass of benzene recovered in the impinger bottle.

The benzene yield stabilised and was within the range of 3 – 6 wt.% of fed toluene for the first 20 min of feeding (Fig. 8). At this initial region, both ratios (Eq. 7 and 8) have similar values, because of high toluene conversion levels. The levelling off of ratios suggest a constant benzene formation pathway at short feeding times. Further toluene feeding increases both ratios, however *B/T fed* ratio increase is less significant than *B/T converted* ratio. This indicates that while the toluene decomposition (a sum of all conversion pathways) becomes less effective with time, the pathway resulting in toluene to benzene conversion is gaining significance.

Benzene formation dependency on different temperatures is more complicated (Fig. 9) than the dependency described previously. It was studied at a constant 10 min feeding time. With the initial temperature increase, benzene yield increases significantly. In the region of 650 – 750 °C, where the toluene conversions are very poor, the difference between the *B/T fed* and *B/T converted* ratios are particularly large. Two factors could explain the increased benzene yield at lower temperatures, namely 1) dealkylation of toluene with hydrogen is a strongly exothermic reaction [45] and 2) most of the benzene from toluene formation is a result of methyl with hydrogen substitution [11]. This suggests that dealkylation of toluene is less temperature dependent than other toluene conversion pathways. At higher temperatures, benzene yield drastically decreases, although it again reaches higher values when feeding times are prolonged (Fig. 8). Both B/T ratios at 800 and 850 °C have similar values.

Fig. 4, Fig. 5, Fig. 8 and Fig. 9 imply that for the six runs with high and constant toluene conversion exceeding 90% (up to 20 min and at least at 800 °C), benzene yield (*B/T fed*) was always low and the share of toluene that was converted to benzene (*B/T converted*) was constant. It can also be noted that these 6 runs correspond with the maximum coke formation. Beyond the 20 min feeding time, coke amounts level off. Also, deposition is significant only at higher temperatures.

It can be observed that benzene formation is enhanced when the coke deposition process is finished or when it does not occur at all. This suggest that the changes in pyrolysis conditions can favour either benzene or soot formation pathways.

Fig. 4. Toluene conversion with toluene feeding time (toluene concentration in the carrier gas was kept constant) at 800 °C

Fig. 5. Toluene conversion with reaction temperature for 10 min feeding time

Fig. 6. Ash content in spent AC from runs with different feeding times at a constant temperature of 800 °C

Fig. 7. Ash content in spent AC from runs at different operating temperatures for a 10 min feeding time

Fig. 8. Benzene yield from toluene conversion for different feeding times at 800 °C

Fig. 9. Benzene yield from toluene conversion at different temperatures with 10 min feeding time

**4. Proposed mechanism**

As it is difficult to unambiguously determine the toluene conversion pathways under these experimental conditions, and the precise role of activated carbon in the pyrolysis mechanism is not known, an assumption of what the most probable toluene decomposition pathways occurs in these experiments is necessary. The undeniable role of AC was confirmed by the fact that tests performed in an empty reactor did not show any toluene conversion products, as well as no (or very insignificant) toluene decomposition, since examined toluene recovery was above 95%.

*Toluene conversion in absence of a catalyst*

Toluene pyrolysis reactions taking place in the gaseous phase were extensively studied and are also most likely to occur up to some extent during these experiments. The first step of toluene pyrolysis is common for all the proposed pathways and involves the decomposition to benzyl and hydrogen or phenyl and methyl radicals. The benzyl-to-phenyl ratio can vary with pyrolysis temperature and pressure, but benzyl creation is always favoured. It is believed that it will further react to yield cyclopentadienyl radicals, mainly through the fulvenallene intermediate, producing acetylene and propargyl radicals in a final step of decomposition [11]. Benzene formation occurs mainly by radical substitution of toluene’s methyl group with a hydrogen atom. Other benzene yielding pathways may include hydrogen radical to phenyl addition or a reaction between two propargyl radicals. However, most of these pathways were reported for higher temperatures above 900 °C and different pressures from 0.01 to 10 atm [8, 11, 15].

*Toluene conversion in the presence of a catalyst*

As previously stated, activated carbon acts as a catalyst in toluene decomposition. In this study, temperatures were insufficient for toluene conversion unless AC was present, since no gas-phase reactions were detected in an empty reactor. Therefore, AC is expected to play an important role in toluene pyrolysis, not only serving as a physical adsorbent for toluene molecules but also as a catalyst in the radical decomposition of toluene. AC is known to provide active sites that can enhance heterogeneous toluene decomposition [3]. Metal species can act as active sites on which hydrocarbons can be adsorbed and rearranged in conjunction with metal reduction [46]. Functional groups can also act as active sites by reacting directly with hydrocarbons. It is also possible that they can be a source of free radicals that participate in gaseous reactions. Since oxygenated groups tend to be released during heating with the first carboxylic groups evolving even below 300 °C [33, 38, 47], it is possible that functional group rearrangement could release some free radicals, or gas-phase olefins. These can further react with toluene, enhancing its decomposition [48].

Gas phase toluene demethylation (Reaction no 3) resulting in benzene creation can be enhanced by new radicals being released from AC surfaces. There might also be new heterogeneous, direct toluene-AC interactions. Additionally, solid carbon is well known to play a significant role in coke formation due to its high surface area and numerous active sites [3, 41, 44, 49, 50]. With the presence of an activated carbon bed, it is difficult to predict how many new toluene conversion pathways are introduced to the gaseous phase mechanism. Therefore, even at the lower temperatures, toluene decomposition is greatly enhanced. Especially, as compared to experiments conducted without a catalytic bed at 800 °C, where toluene recovery was 95% and no liquid conversion products were found.

*Benzene and soot formation competition*

When no catalyst is present, coke/soot formation from hydrocarbons is usually explained by three different mechanisms. In high temperature pyrolysis, e.g. during shock-tube studies or in acetylene flames, the HACA mechanism is the dominating one. At lower temperatures, and in the reactions were acetylene is not as abundant, PAHs creation is ascribed to either cycopentadienyl radical addition or to phenyl addition and cyclisation. In this work temperatures were substantially lower and no soot was formed when experiments were performed in an empty reactor. It was observed that soot inception and growth is enhanced by the presence of a catalyst bed, but it has not been determined, which of the proposed mechanisms is dominant with heterogeneous PAHs formation on the carbon surface at relatively low temperatures (up to 850 °C). Despite the lack of kinetic models and exact mechanism of coking on the AC surface, all known PAHs formation pathways can explain the diminished benzene yield while coking takes place (Fig. 10). The main competitive reactions to direct conversion of toluene to benzene are the formation of benzyl and phenyl radicals. Further participation of these radicals and their derivatives (c-C5H5, C3H3, C2H2) in PAHs formation will most likely shift the equilibrium of toluene decomposition products towards the formation of radicals, supressing direct conversion to benzene. Also, the reversible conversion reaction of phenyl to benzene will shift towards phenyl formation as it will be constantly depleted from the gaseous phase by coking. Therefore, direct benzene from toluene formation and benzene creation from phenyl will be inhibited while larger PAHs are being formed. It is also possible that already formed benzene will be further decomposed to form phenyl and consequently larger PAHs. This assumption would be supported by experiments reported by Shukla et al. [13] where addition of benzene to toluene conversion experiment enhanced PAHs formation at the expense of benzene that was decomposing to phenyl radicals. Moreover, in their runs with solely toluene pyrolysis, the reported yield of the created benzene was diminished at higher temperatures where toluene conversion was almost complete. This might suggest that the created benzene decomposes as there is a decrease of toluene derived radicals. Another pathway for benzene creation, described by Zhang et al. [11], is through the recombination of two propargyl radicals (C3H3) although C3H3 can still take part in PAHs formation, which diminishes benzene yield.

*Activated carbon influence on soot formation*

Besides the known PAH formation pathways, studied in the gaseous phase, another probable toluene removal mechanism involves direct toluene adsorption on a highly porous structure of AC and its active sites. It is also plausible, that toluene rearrangement reactions on AC active sites will lead to soot formation and new species release, e.g. hydrogen (Fig. 11). These types of interactions are observed in many cases [2, 3, 30, 51] yet no detailed mechanism has been proposed so far. AC presence is undoubtedly important in soot formation and it is likely that even reactions typically observed in the gaseous phase (HACA, PAC, c-C5H5 addition) can proceed on the aromatic carbon matrix [19, 47]. Simultaneously some other coking reactions involving functional groups and metals on the AC surface can occur [2, 3], possibly more significant since the deactivation of AC is observed when its surface gets hindered by coke.

As previously noted in section 3, coke production decreases with time and eventually plateaus. A decrease in the coking reaction rates will most likely shift the equilibrium between benzene, phenyl and benzyl towards benzene creation, as indicated by an increase in benzene production after coking finishes.

High benzene yields recovered during lower temperature runs suggest that while these experimental conditions are not adequate for coke formation, toluene dealkylation proceeds with relatively high efficiency. Also, after the AC passivation with coke, benzene yield increases. This in turn suggests that constantly fed toluene continuous to be converted to benzene, regardless of the lack of available AC active sites. Additionally, for runs when toluene was fed in the absence of AC, dealkylation did not occur. Therefore, it can be expected that the initialization of radical reactions by the AC surface is essential in the dealkylation process. Moreover, it is possible that even a deactivated, soot-covered surface can take part in toluene to benzene conversion while it no longer shows catalytic effects on coke formation.



Fig. 10. Diagram of the most probable toluene conversion pathways. Filled arrows indicate reactions favouring coke formation and therefore lowering benzene yield.

# 5. Conclusions

In this work toluene pyrolysis in the presence of activated carbon as a catalyst was studied. Experiments were carried out in an inert flow of N2 at 1 atm overpressure, and at temperatures up to 850 °C. Such conditions were inadequate for toluene to decompose if the AC was not present. The main issues concerning toluene conversion over solid carbon, that were confirmed or raised as a result of this work were:

* In the studied conditions AC is necessary for toluene decomposition initiation and propagation. The AC role might be just to serve as an adsorbent due to its functional groups but more likely it is also a source of free radicals that are released from its surface during the heating up.
* Soot/coke deposition on the AC surface is observed only at higher temperatures of at least 800 °C.
* Toluene decomposition throughout coking is necessary to maintain high conversion levels. It is therefore crucial to maintain coke deposition throughout the whole process, which in turn requires constant coke gasification achieved by the addition of an oxidising agent. Other conversion pathways are also present and some toluene conversion is still maintained after the coking ceases, yet high conversion rates are only achieved while coke is depositing on the surface of AC.
* Soot and benzene are created in competing pathways. Enhanced soot formation suppresses toluene to benzene conversion. If coking is finished or does not occur at all, benzene yield increases significantly.
* Toluene conversion to benzene can undergo even after AC deactivation with coke, however carbon presence was necessary to start toluene conversion. Therefore, it can be assumed that the dealkylation is either initialised in the gas phase by radicals released from the AC so the reaction propagates after the surface deactivation or that it can undergo heterogeneously on the carbon surface, even if it is covered with an inactive soot layer.

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