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FORMATION MECHANISM OF AROMATIC MOLECULES IN FLAMES

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Abstract

The formation of first-benzene aromatic rings occurs at the same reactionary routes all flames (acetylene, ethylene, and propane), after the decomposition of fuel and formation of aromatic precursors. It has been found that the reaction routes dependent on temperature. To low temperatures, T<1500K dominate routes that include the formation of C_2H_3 from C_2H_2, and further C_4H_5, which in reaction with C_2H_2 gives C_6H_6. To high temperature is dominated the formation reaction of propargyl (C_3H_3) and the main reaction formed the benzene is propargyl.

Keywords: mechanism, flame, acetylene, ethylene, propane.

Introduction

The process of soot formation has been the object of numerous investigations for more than 100 years [1,2], and such investigations did not loose their significance to the present day. This is explained, first of all, by the fact that soot is an industrial product produced on a world scale in the amount of 10^7 tons a year. The black (technological) carbon is used as a filler of elastometers (90 % of the technological carbon is used for this purpose, and 2⁄3 of it – in the production of tires) and has a wide application in printers. However, soot is a carcinogenic pollutant of the environment, formed as a result of the combustion of hydrocarbon fuels in power plants and engines. For example, diesel engines with direct fuel injection initially transform approximately 10-20 % of the fuel introduced into the soot. Simultaneously with the soot formation, fullerenes and nanotubes are formed by the mechanism competing with the mechanism of soot formation. A knowledge of the conditions and mechanisms of formation of soot, fullerenes, and nanotubes in a flame allows one to change the combustion such that soot particles, fullerenes, or nanotubes are predominately formed.

At the present time a large number of experimental data on the processes of soot formation have been accumulated and different phenomenological models have been proposed [3,4]. However, the mechanism of soot formation is imperfectly understood yet. This is explained by the fact that even in simple cases, such as the homogeneous pyrolysis of hydrocarbons, this process includes a large number of rapid simultaneous reactions leading to the formation of a new solid phase – soot particles (e.g., the time of transformation of methane with a molecular mass of 16a.m.u into the soot with the molecular mass more than 10^6 a.m.u makes 10^{-4}–10^{-2}s) [5].

The formation of the polyaromatic precursors in flames is a key element in the process of soot formation. The reaction path of formation of these precursors, primarily C_2H_2, C_3H_3, C_3H_4, C_3H_5, depends on the type of the fuel and parameters of the flame. Although the formation of polyaromatic molecules and soot in the combustion process of fuels intensively have been studied, the final kinetic scheme has not worked out, requires further optimization and refinement of kinetic parameters.

Design and operation of gas turbines and engines are very sensitive to the underlying fuel chemistry. Practical fuels are complex mixtures of several hundreds of individual species, which can be divided in four hydrocarbon families (*n-/i-* paraffins, naphthenes (cycloparaffins) and aromatics), Fig.1. The number of different isomers increases significantly moving towards large hydrocarbons increasing dramatically the size of detailed kinetics models. The kinetics of all of the fuel components and intermediate species are not fully determined and investigated. Therefore, only simplified reaction models of practical fuels - surrogate blends or reference fuels, which represent the real fuels chemical kinetics with a small num-

ber of components in the input formula of the surrogate - can be used presently in the CFD modelling and design of combustion chambers. The surrogate includes adequate fractions of different hydrocarbons which are present the different chemical families of fuels [6]. The reaction kinetic model of the surrogate should be constructed from sub-models of each individual component contained input formula of the surrogate.

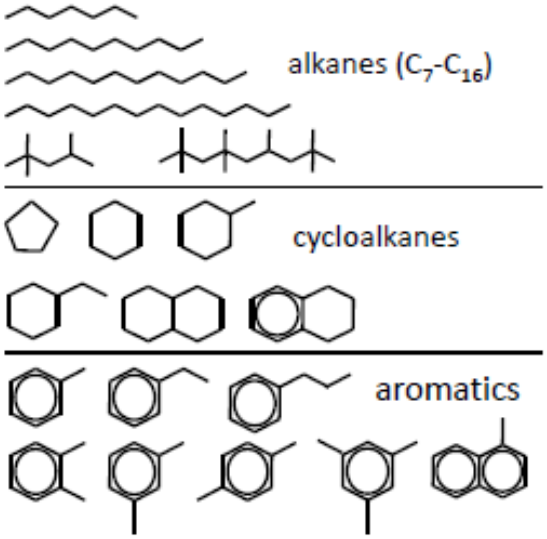

Fig.1 – Four families of hydrocarbons involved in practical fuels [6]

The present work is devoted to investigation of the flame of acetylene, ethylene and propane with aim to determine features of the formation of the first aromatic ring (benzene, A1, C_6H_6) in flames of saturated (C_3H_8) and unsaturated (CH≡CH, CH_2=CH_2) hydrocarbons.

Kinetic model

On the basis of existing detailed kinetic schemes [6,7] a general and consistent mechanism of the oxidation of hydrocarbons and the formation of higher hydrocarbons was compiled for computational studies covering the characteristic properties of a wide range of combustion processes. Computed ignition delay times of hydrocarbon–oxygen mixtures (C_2H_2 [8], C_2H_4 [9,10], and C_3H_8 [10]) match the experimental values. The calculated absolute flame velocities of laminar premixed flames (C_2H_2 [11,12], C_2H_4 [11], and C_3H_8 [13]) and the dependence on mixture strength agree with the latest experimental investigations reported in the literature. With the same model concentration profiles for major and intermediate species in fuel-rich, sooting, premixed C_2H_2, C_2H_4 and C_3H_8 air flames are predicted in good agreement with experimental data. An analysis of reaction pathways shows for C_2H_2 and C_3H_8 flames that benzene formation can be described by propargyl combination in high temperature.

Numerical modelling was performed using the SENKIN (for simulation of ignition delay time) and PREMIX (for simulation of laminar flame speed, species concentration profiles and sensitivity analysis) code from the CHEMKIN II package [14] and Chemical Workbench [15].

Results

Acetylene flame (acetylene/oxygen/argon flame φ =1.93, at 0.05 atm)

Figure 2 presents the results of experimental and numerical measurement of laminar flame speed of premixed acetylene - oxygen mixture. Figure 2 shows that the results of the simulation with mechanism [6] can be regarded as satisfactory in the area of the poor and stoichiometric, also in area of the fuel rich ($\varphi > 1.5$). The greatest error occurs for the rich flames in the range $1.6 < \varphi < 2.0$, where the differences in the results of the experiment and numerical simulation of up to 30%. This problem was also observed in [16].

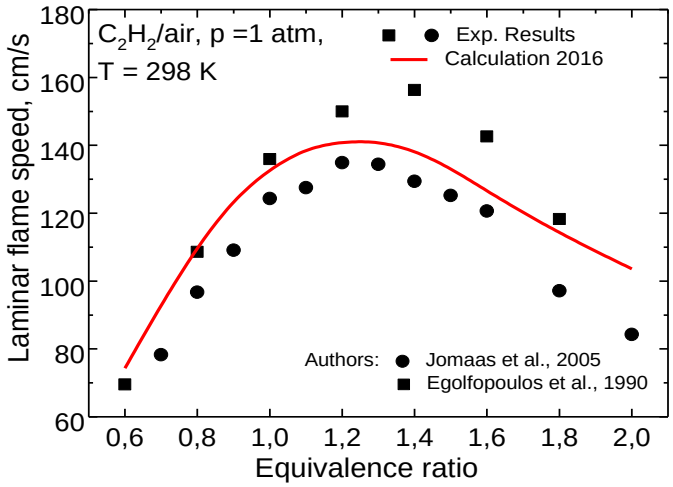

Fig.2 – Experimental (closed symbol) and computed (line) laminar flame speed of C_2H_2 flame

As seen in Figure 2, the authors of the experimental data [11] and [12] differ in rich flames in the range $1.4 < \varphi < 2.0$. This may be due to experimental measurement errors.

In the Figure 3 are shown the numerical of ignition delay time of the acetylene - oxygen mixture with the addition of argon, the results are in satisfactory agreement with the experimental data.

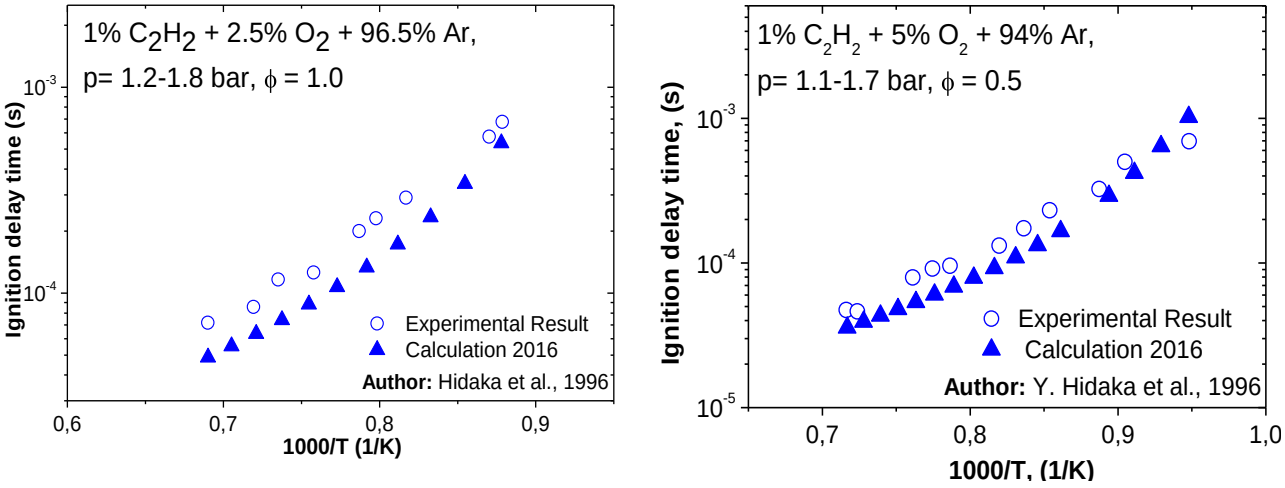

Fig.3 – Experimental (closed symbol) and computed (open symbol) ignition delay time of C_2H_2 flame

In Figure 4 shows the mole fraction profiles of these stable compounds and intermediate species: C_3H_3 (H_2CCCH), C_3H_5, C_4H_5, A1. As seen in Figure 3, the model describes in good agreement with experimental results these main components: C_3H_3 (H_2CCCH) and A1.

Although, the mechanism shows inflated values of the mole fractions of intermediate species: C_3H_5 и C_4H_5.

Sensitivity analysis identifies the rate-limiting reaction steps. The rates of the elementary reactions in combustion process differ greatly. Sensitivity analyses show that only a few elementary reactions are rate-limiting.

Other reactions are so fast, that the accuracy of the rate coefficients has a minor influence on the simulation of the overall combustion process [17].

Reaction sensitivity analysis for acetylene/oxygen/argon flame at the temperature (950 and 2100 K) is shown in Figure 5.

As seen analysis the main reaction, which influenced to formation C_6H_6 at the temperature 950 K, is $C_6H_6 = C_4H_4 + C_2H_2$, and for temperature 2100 K is $C_2H_2 + CH_3 = C_3H_5$.

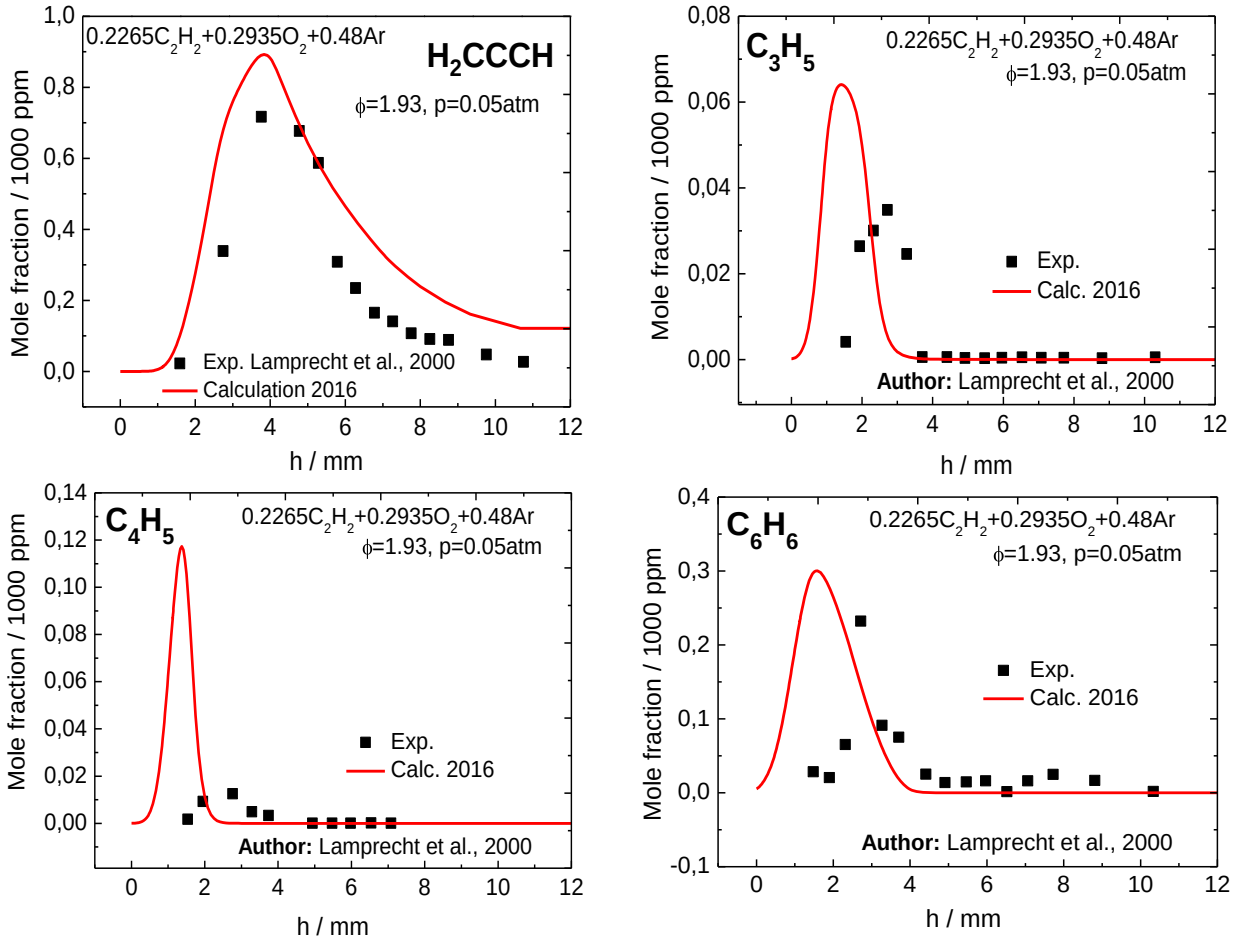

Fig. 4 – Experimental (symbol) and computed (line) mole fraction profiles of C_3H_3 (H_2CCCH), C_3H_5, C_4H_5, A1 in acetylene/oxygen/argon flame

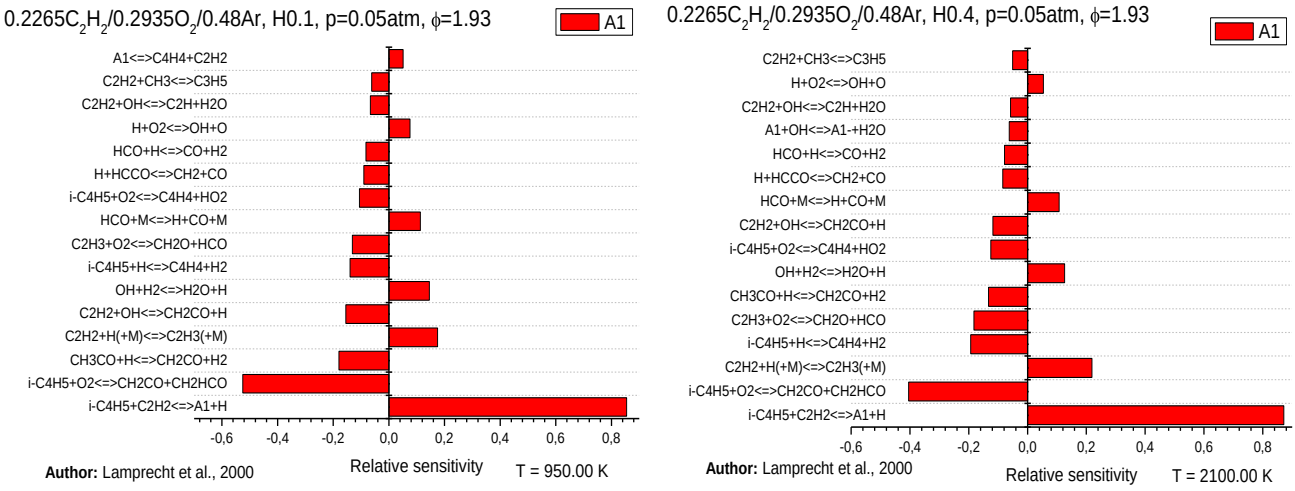

Fig.5 – Reaction sensitivity analysis for acetylene/oxygen/argon flame at the temperature (950 and 2100 K)

Figure 5 shows the route of the reaction pathways of benzene formation (A1) in a flame of acetylene (C_2H_2). As shown, the sensitivity analysis of the formation of the first aromatic ring-benzene in acetylene flame can be carried out in two ways: at low temperatures (T <1500 K) and high T>1500K temperatures.

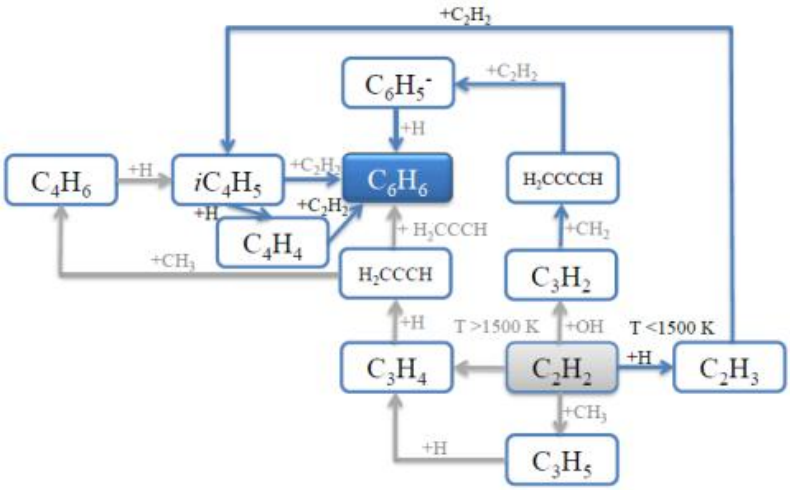

Fig. 6 – Reaction paths from acetylene to benzene [18]

Route-formation of the first aromatic ring-benzene at low temperatures can be produced as follows: 3 different intermediate molecules such as C_3H_2, C_3H_4, C_3H_5, formed from acetylene; followed by the formation of propargyl followed by the formation of benzene. This is the main way of educating the ring-benzene. This route was also considered in [16] as a primary way of benzene formation. Route-formation of the first aromatic ring-benzene at high T>1500 K temperature can be produced as follows: acetylene forms C_2H_3 radical, followed by the formation of intermediate molecules iC_4H_5 and/or C_4H_4 that lead to the formation of benzene (A1).

Ethylene flame (ethylene/oxygen/argon flame φ =3.06, at 1 bar)

Figure 7 shows the results of the experimental and calculated measuring the laminar flame speed of premixed flames ethylene-oxygen-argon mixtures. The experimental results are in satisfactory agreement with the calculated results.

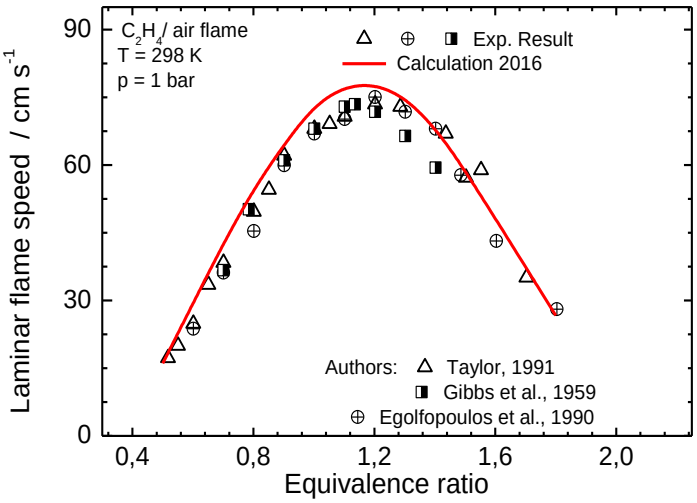

Fig.7 – Experimental (closed symbol) and computed (line) laminar flame speed of C_2H_4 flame

In order to prove the quality of the presented mechanism and its general applicability this scheme was chosen without further modifications for the calculation of ignition delay times of ethylene flame. As demonstrated in Fig. 8 the absolute values and the temperature dependence of the experimentally determined ignition delay times are well reproduced by the calculations. It is noteworthy to state that the original Baker [19] scheme gave similar results with minor deviations for ethylene - oxygen mixtures.

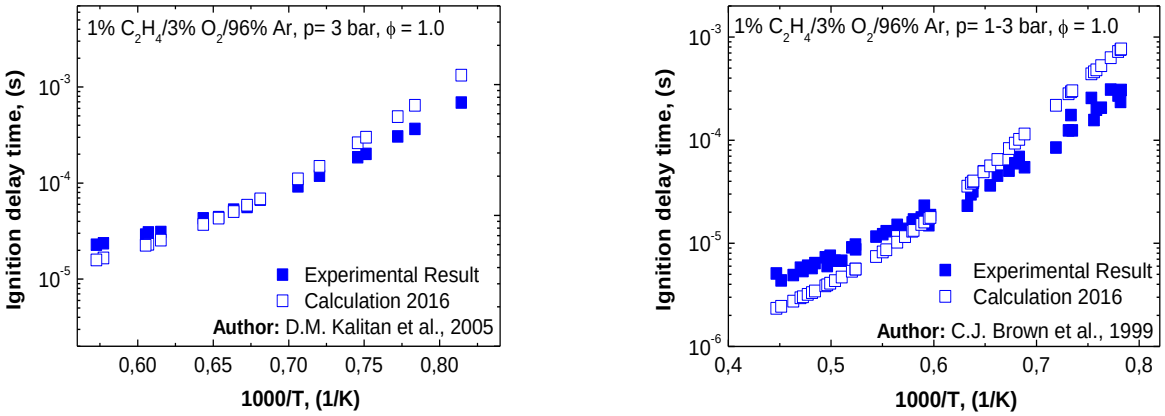

Fig.8 – Experimental (closed symbol) and computed (open symbol) ignition delay time of C_2H_4 flame

In Figure 9 shows the mole fractions profile of these stable compounds: C_2H_2, C_4H_4, A1, A2. As seen in Figure 8, the model describes in agreement agreements with the experimental results of the concentration of C_2H_2, C_4H_4, A1 и A2.

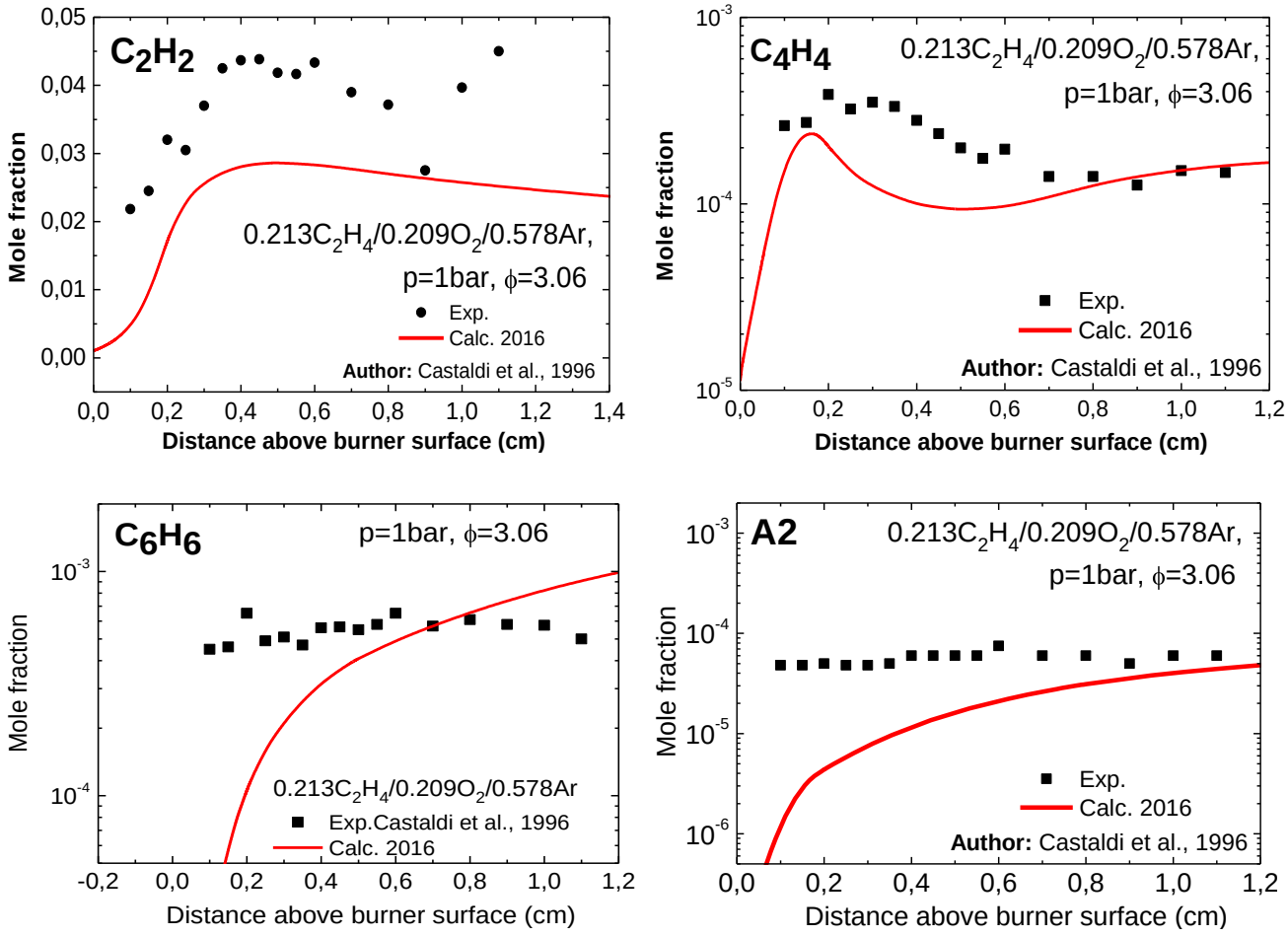

Fig. 9 – Experimental (symbol) and computed (line) mole fraction profiles of A1, A2, C_2H_2, C_4H_4 in ethylene/oxygen/argon flame

For the flame of ethylene is characterized by low temperatures. Figure 10 shows a sensitivity analysis of the reaction to the flame of ethylene (C_2H_4) (φ = 3,06) at low temperature 865.56 and

1419.58 K. As the analysis at 865.56 K, the main reaction is $iC_4H_5 = C_2H_3 + C_2H_2$, and for the temperature of 1419.58 K is determined by the reaction $iC_4H_5 + O_2 = C_4H_4 + HO_2$.

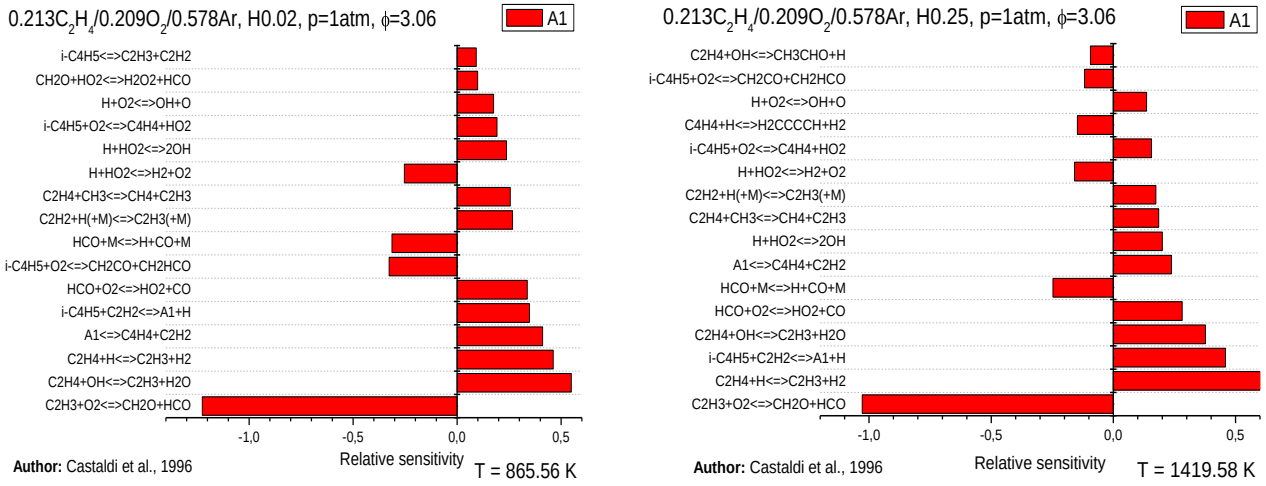

Fig.10 – Reaction sensitivity analysis for ethylene/oxygen/argon flame at the temperature (865.56 and 1419.58 K)

Fig. 11 illustrates the reaction pathway of benzene C_2H_2 flame at low temperatures (T<1500 K). As can be seen from the diagram, the ethylene forms an intermediate molecule C_2H_3 which form the acetylene. So, acetylene is added another molecule of acetylene and forms an intermediate molecule iC_4H_5. This intermediate molecule iC_4H_5 adds another molecule acetylene and forms ring-benzene. This is one way the formation of ring-benzene.

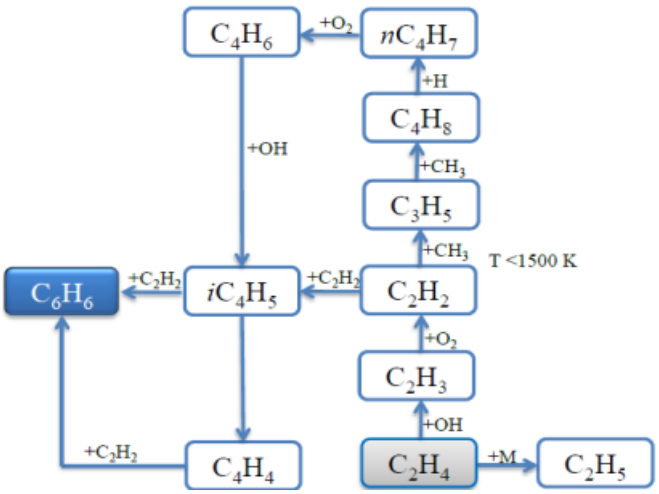

Fig. 11 – Reaction paths from ethylene to benzene [18]

The second way is this - acetylene adds $\cdot CH_3$ radical and radical forms $\cdot C_3H_5$, which forms an intermediate molecule C_4H_8 then formed nC_4H_7. Radical adds oxygen molecules and form an intermediate molecule C_4H_6 and this molecule forms intermediate molecule iC_4H_5. As was found in the sensitivity analysis the way that has been described above, the formation of through iC_4H_5, ring-benzene, and benzene ring may be formed via an intermediate molecule C_4H_4, as shown in the scheme.

Propane flame (propane/oxygen/argon flame φ =2.6, at 1 atm)

Figure 12 shows the results of the experimental and calculated measuring the laminar flame speed of premixed flames of propane-oxygen-argon mixtures.

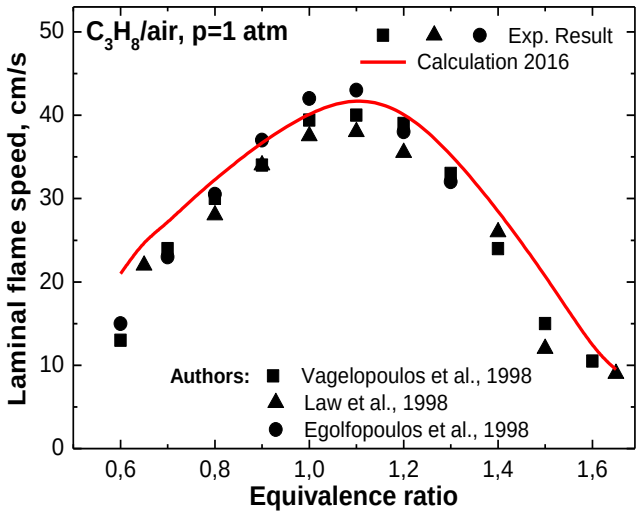

Fig.12 – Experimental (closed symbol) and computed (line) laminar flame speed of C_3H_8 flame

Figure 12 shows that the simulation results with the mechanism [9] can be considered satisfactory in stoichiometric flames, as well as in a large excess of combustible material (φ >1.6). The greatest error occurs for the poor flames in the range of φ = 0,6, where the differences reach 25% in the results of the experiment and numerical simulation.

In the Figure 13 are shown the numerical of ignition delay time of the propane - oxygen mixture with the addition of argon, the results are in satisfactory agreement with the experimental data.

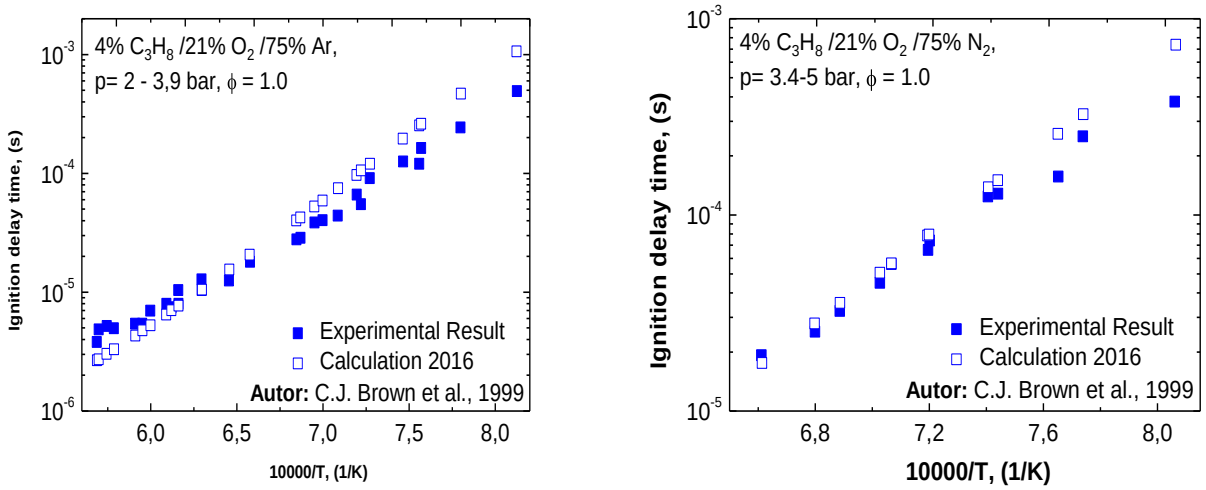

Fig.13 – Experimental (closed symbol) and computed (open symbol) ignition delay time of C_3H_8 flame

To propane flame (propane/oxygen/argon flame φ = 2.6, at 1 atm) to simulate the measured concentrations of molecules and radicals (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_4H_2, C_4H_4, C_3H_5), involved in the formation of aromatic rings, as well as aromatic molecules A1 (C_6H_6) and A2 ($C_{10}H_8$), Fig. 14. The model predicted very well C_3H_8, O_2 and H_2O concentrations for 0.2-0.6, 0.35-0.6 and 0.2-0.4 distance above burner surface, respectively. The H_2O concentrations are underpredicted between 0.0-0.2 and 0.4-0.6 distance above burner surface. The model very well described CO_2 concentrations for all distance. Measured and simulated concentration profiles of intermediate molecules CH_4, C_2H_2, C_2H_4,C_2H_6, and radicals C_3H_4, C_4H_2,C_4H_4,C_3H_5, involved in aromatic ring formation, as well as the aromatic molecule C_6H_6 and A2 are shown in Fig. 14.

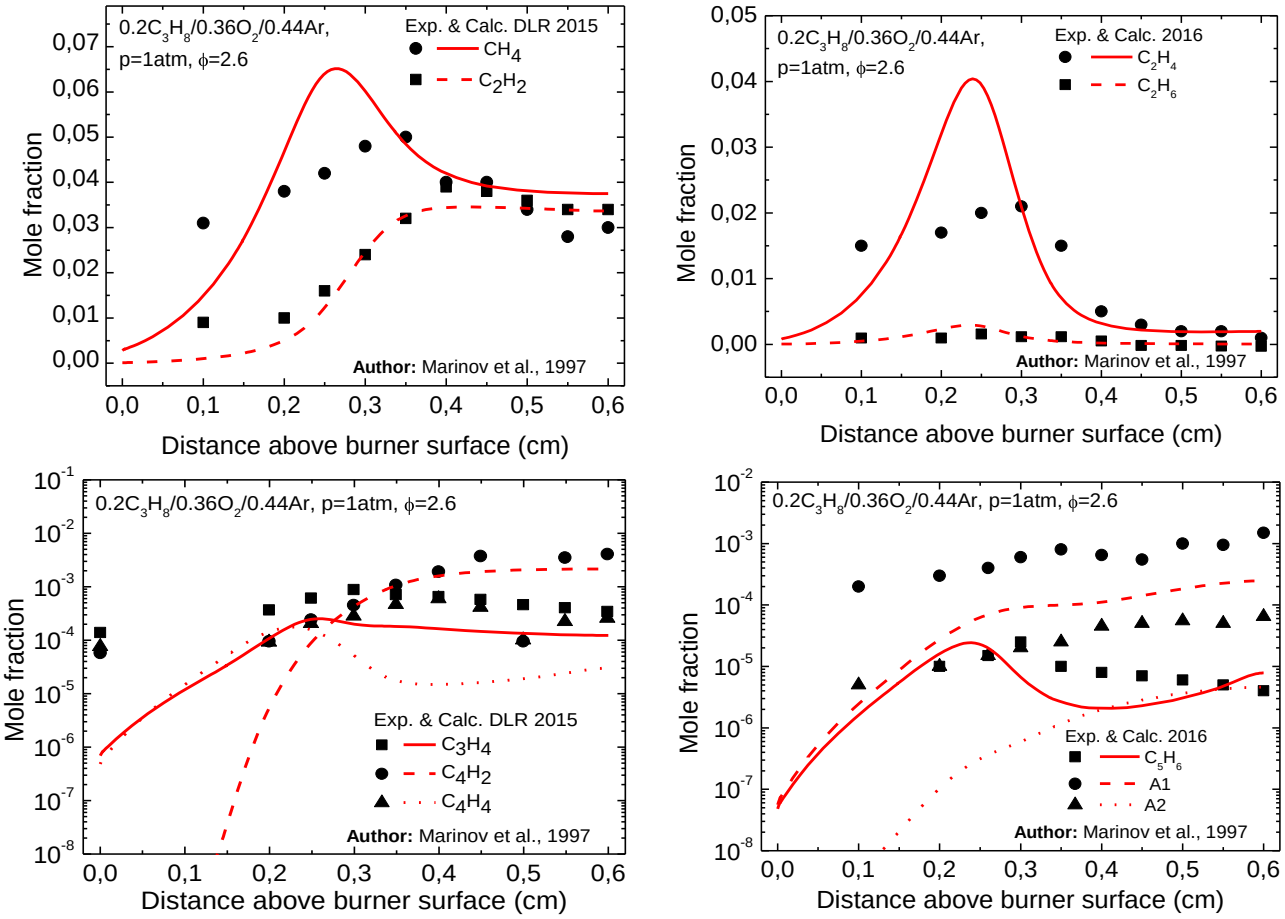

Fig. 14 – Experimental (symbol) and computed (line) mole fraction profiles of CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_4H_2, C_4H_4, C_5H_6, A1, A2 in propane/oxygen/argon flame

The model fairly well predicted methane, acetylene and ethane concentrations in a premixed propane-oxygen-argon flame. The model predicted ethylene concentration to two times higher than the measured data, although the post flame zone is predicted quite well. The C_3H_4, C_4H_2 and C_4H_4 concentrations were quite well predicted in the post reaction zone although the model underpredicted in the preheat zone.

The calculated concentrations of benzene and naphthalene are also lower than the experimental values, but are within a predetermined error.

Figure 15 shows a sensitivity analysis of the reaction of ethylene flame (C_2H_4) (φ = 2.6) at a temperature of 848 K and 1607.70 As show the analysis for temperatures 848 and 1607.70 For the main reaction is $C_2H_2 + H + (+M) = C_2H_3 (+M)$.

Fig. 16 illustrates the reaction pathway of benzene formation in flame of propane (C_3H_8).

From these schemes, it follows that the formation of the first aromatic ring-benzene happens after the expansion has occurred and the operating time of the fuel aromatic precursors. The reaction routes depend on the temperature. To the low temperatures T <1500 K for propane flame is dominated by routes which involve the formation of *i(n)*C_3H_7, C_2H_5 and further C_4H_5, which in final reaction gives C_6H_6 (A1). To high temperature is dominated by reaction to form propargyl and the main reaction is the reaction of the formation of benzene formation propargyl.

Conclusion

• Developed reaction mechanism describes the PAH formation in laminar premixed flame of saturated (C_3H_8) and unsaturated (C_2H_2,C_2H_4) hydrocarbons;

• The main parameter influenced first aromatic ring formation is temperature (T), independent of molecular structures or pressure;

• At T<1500 K the main aromatic precursors are iC_4H_5, C_4H_4; at T>1500 K dominated pathway to aromatic ring is H_2CCCH recombination.

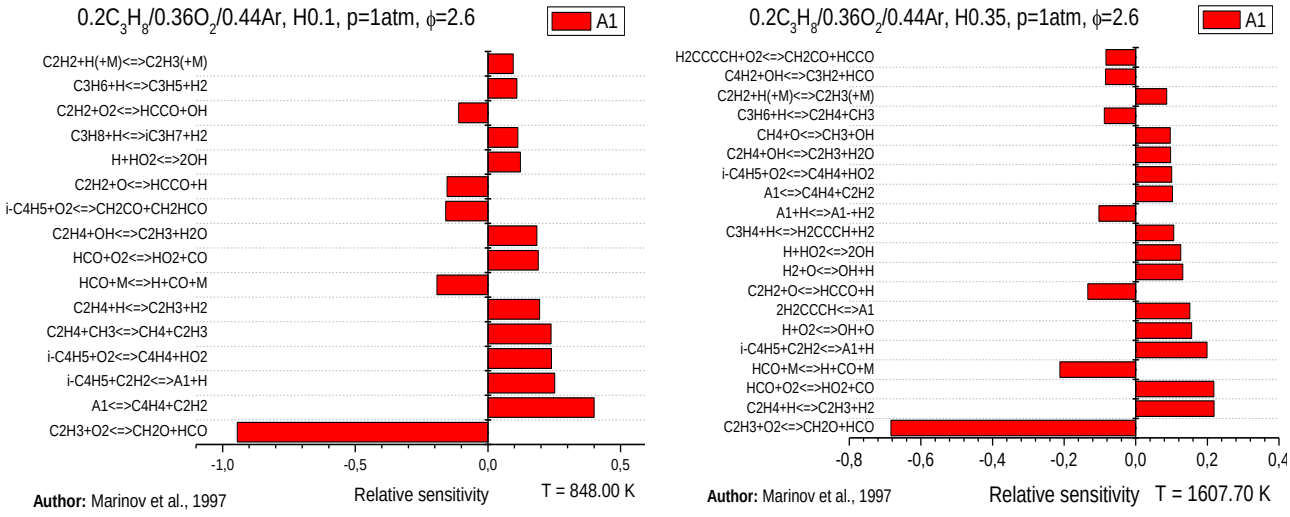

Fig.15 – Reaction sensitivity analysis for propane/oxygen/argon flame at the temperature (848.00 and 1607.70 K)

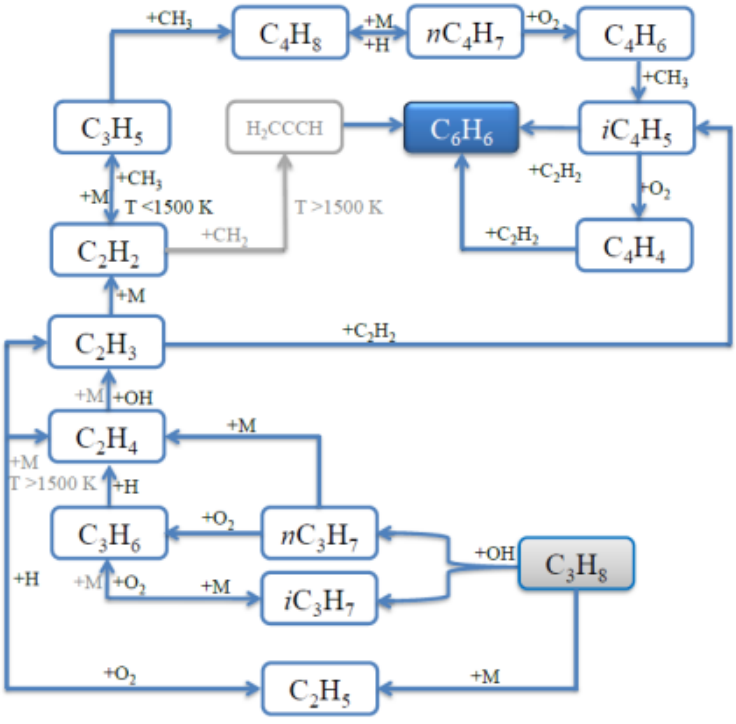

Fig. 16 – Reaction paths from propane to benzene [18]

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МЕХАНИЗМ ОБРАЗОВАНИЯ АРОМАТИЧЕСКИХ МОЛЕКУЛ В ПЛАМЕНИ

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Аннотация

Образование первого ароматического кольца-бензола происходит по аналогичным реакционным маршрутам во всех пламенах, после того как произошло разложение топлива и наработка ароматических прекурсоров. Было установлено, что реакционные маршруты зависят от температуры. Для низких температур, T<1500K, доминируют маршруты, которые включают образование C_2H_3 из C_2H_2, и далее C_4H_5, который в реакции с C_2H_2 дает C_6H_6. Для высоких T доминируют реакции образования пропаргила (C_3H_3) и основной реакцией образования бензола является реакция образования пропаргила.

Ключевые слова: механизм, пламя, ацетилен, этилен, пропан.

ЖАЛЫНДА АРОМАТТЫ МОЛЕКУЛАЛАРДЫҢ ТҮЗІЛУ МЕХАНИЗМІ

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Аннотация
Отынның толық ыдырауынан кейін және ароматты прекурсорлардың түзулуінен кейін барлық жалындарда бірінші ароматты сақина-бензолдың түзілуі бір маршрутпен жүреді. Реакциялық маршруттар температураға тәуелді екені анықталды. Төменгі температулар үшін, T<1500K, C_2H_3 және C_2H_2 радикалдарының одан кейін C_4H_5 радикалдарының ацетилен C_2H_2 молекуласымен әрекеттесіп C_6H_6 молекуласының түзілуі басыңқы келеді. Жоғары температураларда пропаргил (C_3H_3) молекуласынан бензол молекуласының түзілуі басыңқы және бензол алудың ең маңызды жолы осы жол болып табылады.
Түйінді сөздер: механизм, жалын, ацетилен, этилен, пропан.