

## **Oligomerization of acetylene from gas electrocracking over Pd/CNFs catalyst**

**البلمرة المحددة للاستيلين الناتج من غاز التكسير الكهربائي  
على العامل المساعد Pd/CNFs**

علي سامي أسماعيل

قسم الكيمياء- كلية التربية للعلوم الصرفة – جامعة الانبار - العراق

E-mail: chemocenter@gmail.com

### **Abstract**

The unique properties of carbon nanofibers (CNFs), a novel structured carbon material developed in the last two decades, have generated a large number of applications including selective absorption, energy storage, polymer reinforcement, and catalyst supports.

The results show the possibility production of olefin hydrocarbons from gas electrocracking as a first stage, and the subsequent stage investigated the regularities of the oligomerization of acetylene in the gas electrocracking on palladium catalyst, we supported palladium on CNFs and developed a highly active catalyst for hydrogenation of hydrocarbons. CNFs supported palladium catalysts (0.5%Pd) were prepared by a standard incipient impregnation method using aqueous solutions of palladium (II) chloride PdCl<sub>2</sub> as a palladium precursor. Carbon nanofibers (CNFs) were synthesized from a previous study to us, obtained also from acetylene in the gas electrocracking over  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst, oligomerization of acetylene with a Pd/CNFs catalyst has been investigated. Catalytic experiments were performed in a fixed bed reactor at atmospheric pressure, synthesized at (140 – 270) °C, using gas hourly space velocity (GHSV) in the range (3000-7000) h<sup>-1</sup> of feed gas. Resulting shows that the yield of green oil or (liquid hydrocarbons) reduce when the temperature increase and increase in the yield of methane, ethene, propene and butene, as well as a more stable catalyst.

**Keywords:** carbon nanofibers (CNFs), olefin hydrocarbons, gas electrocracking, oligomerization, Pd/CNFs catalyst, atmospheric pressure, gas hourly space velocity (GHSV), green oil

### **الخلاصة**

يمتلك الكربون الليفي الدقيق (CNFs) (Carbon nanofibers) خصائص فريدة من نوعها ، وبحكم تركيبه الجديد ، فإن المواد الكربونية أظهرت تطورا في العقدين الماضيين . لقد وجد أن المواد الكربونية لها عدد كبير من التطبيقات المتضمنه الامتصاص الانتقائي، تخزين الطاقة، مواد لتعزيز البوليمرات وكحوامل للعوامل المساعدة . وأظهرت النتائج إمكانية إنتاج مواد هيدروكربونية أوليفينية من غاز التكسير الكهربائي كمرحلة أولى ، وتتضمن المرحلة اللاحقه التحقق من أنظام البلمرة المحددة للاستيلين الناتج من غاز التكسير الكهربائي على العامل المساعد البلاتينيوم . لقد استخدمنا الكربون الليفي الدقيق كحامل للعامل المساعد البلاتينيوم ، حيث أظهر العامل المساعد الفعالية العالية في هدرجة الهيدروكربونات .

تم تحضير (Pd 0.5%) من البلاتينيوم المحمول على الكربون الليفي الدقيق بطريقة الاشباع الاولي القياسي باستخدام محلول مائي من كلوريد البلاتينيوم (PdCl<sub>2</sub>) (II) كمصدر للبلاتينيوم. بينما تم تحضير الكربون الليفي الدقيق من دراسة سابقة لنا . حيث تم تحضيره أيضا من الاستيلين الناتج من غاز التكسير الكهربائي باستخدام العامل المساعد  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> ، وبذلك تم إنجاز البلمرة المحددة للاستيلين مع العامل المساعد Pd/CNFs. التجارب المختبرية تم إجراءها على مفاعل ذو سرير ثابت ، وعند الضغط الجوي الاعتيادي ، وبدرجات حرارة تتراوح (140-270 °C) ، وبأستخدام السرعة الحجمية لغاز التغذية بالساعة (غاز التكسير الكهربائي الحاوي على الاستيلين) بزم من 3000-7000 h<sup>-1</sup>. وتظهر نتائج الدراسة انخفاض ناتج الزيت الأخضر (الهيدروكربونات السائلة) عند زيادة درجة الحرارة، ويقابله زياده في ناتج الميثان والايثلين والبروبلين والبيوتيلين بالإضافة الى أستقرار العامل المساعد .

### **مفتاح الكلمات**

الكربون الليفي الدقيق (CNFs) ، هيدروكربونات اوليفينية ، غاز التكسير الكهربائي ، البلمرة المحددة ، العامل المساعد Pd/CNFs، الضغط الجوي الاعتيادي، السرعة الحجمية لغاز التغذية بالساعة، الزيت الاخضر.

## **Introduction**

The synthesis and development of solid-supported metal catalysts has been the subject of most research on catalysis. These catalytic systems have higher reactivity due to their larger active surface area and offer the advantages of heterogeneous catalysis, like ease of handling and recyclability. Nowadays, the development of nano-sized solid supported metal catalysts to make them even more reactive is very popular. For instance, palladium anchored or immobilized on various kinds of supports, such as carbon, clay, silicates, zeolites, amorphous or mesoporous silica, porous biomaterial or polymers, has gained considerable attention due to its remarkable performance in wide range of organic transformations, especially in coupling and in hydrogenation reactions. [1-6]Metals that have a high activity for hydrogenation reactions include Ni, Fe, Rh, Ru, Pd, and Pt, etc [7].Here we present a brief literature review on the kinetics and catalytic aspects of the selective hydrogenation of acetylene/ethene on palladium based a catalyst that is Pd/CNS (Carbon Nanostructures). First, we shall discuss the properties of palladium catalysts with respect to adsorption of hydrogen, acetylene and ethene on the metal surface. After a briefdiscussion on the oligomerization, the literature on the mechanisms and kinetics of the hydrogenation reactions will be reviewed.

## **Properties of Pd/CNF catalysts**

The Pd/CNF catalysts proved to have superior selectivity and activity hydrogenation of acetylene on palladium–nanostructured catalysts, and the Pd/ CNFs showed formed less green oil and no detectable coke formation compared to the commercial catalysts under the experimental conditions [8].Carbon nanofibers are the innovative materials that show potential as catalyst support [9].Compared to activated carbon, CNF present a high specific surface area without microporosity, preventing mass transfer limitations. In addition, their graphitic structure leads to metal-support interaction, which can improve catalytic activity/ selectivity. Up to now, the majority of catalysts based on CNF are used in the form of fine powders. It makes them difficult to handle and provokes high pressure drop though the catalytic bed.

## **Adsorption/absorption of H<sub>2</sub> on Pd catalysts and phase transformations in Pd particles supported on carbon nanofibers**

It is generally accepted that hydrogen adsorbs dissociative on palladium. Adsorption enthalpies have been reported in the range of (24-110) kJ/mol, dependent on many factors such as type of support, impurities, pretreatment.Besides adsorption, absorption of hydrogen can also take place, in particular for unsupported palladium. Two different phases of palladium hydride can be formed: a hydrogen poor  $\alpha$ -phase and a hydrogen rich  $\beta$ -phase. The role of the hydride formation in the hydrogenation has been discussed by a number of authors, but it is not clear whether it is important for industrially applied supported palladium catalysts, which usually have a very low Pd content[10].

If formed, the  $\beta$ -phase has been shown to be more active, but less selective than the more common  $\alpha$  phase. The formation of the  $\beta$ -phase is suppressed by a high metal dispersion. The structural changes induced by exposing ACF (activated carbon fibers) and Pd-ACF to high pressure (up to 10 bar) hydrogen was monitored using in-situ XRD measurements. No changes were detected in the carbon structure after adsorption and desorption cycles at room temperature; however the equilibrium between  $\alpha$ -phases and  $\beta$ - phases of Pd hydride were easily monitored. Figure 1a shows the position and relative intensity of (111) peaks of the two phases as a function of partial pressure of H<sub>2</sub> in mixtures with He. The degree of  $\beta \rightarrow \alpha$  conversion during desorption of hydrogen from 10 bar H<sub>2</sub> is plotted in Fig. 1b as a function of partial pressure of H<sub>2</sub>. For comparison, also shown are similar plots for a reference Pd sponge sample and a commercial Pd on activated carbon catalyst (1% wt Pd from Acros Organics Company). The average size of Pd particles was 47.5 nm in Pd-ACF, 32.5 nm in Pd sponge, and 4.0 nm in the Pd catalyst. The hydrogen pressure corresponding to 50 %  $\beta \rightarrow \alpha$  conversion reflects the stability of the H-rich  $\beta$ -Pd hydride phase. The results show that the decomposition of  $\beta$ -Pd hydride during hydrogen desorption

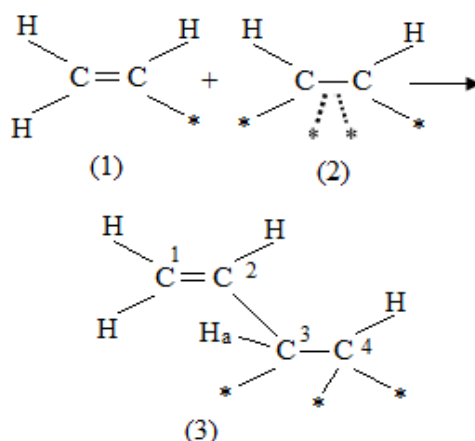
occurs earlier (at a higher pressure) on Pd-ACF in comparison with Pd-sponge and Pd catalyst [11]. This shows that the H-rich Pd hydride phase on Pd-ACF is destabilized by the intimate contact with the activated carbon in Pd-ACF, which has hydrogen adsorption properties by itself. This is indirect evidence that the highly microporous carbon support in Pd-ACF acts like a “hydrogen pump” that causes “leaking” of H atoms from the H-rich Pd hydride phase, as suggested for hydrogen spillover [12]. The higher “pumping efficiency” of the microporous carbon in Pd-ACF is probably the consequence of the preparation method of this material: premixing the Pd salt with the carbon precursor before carbonization produced Pd particles embedded in the carbon matrix with a better metal-carbon contact. In contrast, a less efficient metal-carbon contact is expected when Pd is added after formation of the carbon support (the case of Pd catalyst). These differences are reflected in the order of H<sub>2</sub> pressures that correspond to a 50 % conversion of  $\beta \rightarrow \alpha$  hydride phases: 5 mbar for Pd-ACF, 0.5 mbar for Pd catalyst, and 0.01 mbar for Pd sponge. This study supported the above, as explained the stability of Pd hydride phases in

Results indicate that higher degrees of Pd-carbon contacts for Pd particles embedded in a microporous carbon matrix induce efficient 'pumping' of hydrogen out of  $\beta$ -PdH<sub>x</sub>. It was also found that thermal cleaning of carbon surface groups prior to exposure to hydrogen further enhances the hydrogen pumping power of the microporous carbon support. In brief, this study highlights that the stability of  $\beta$ -PdH<sub>x</sub> phase supported on carbon depends on the degree of contact between Pd and carbon and on the nature of the carbon surface [13].

### **Adsorption of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on Pd catalysts**

For the adsorption of ethene on Pd catalysts different types of adsorbed species have been proposed and both associative and dissociative adsorption can occur. A part of the adsorption was shown to be irreversible [14]. Dissociative adsorption of ethene might be responsible for a self hydrogenation of ethene: hydrogen atoms from dissociative adsorbed ethene can react with associatively adsorbed ethene to form ethane. Different forms of adsorbed ethene that have been shown to exist on Pd catalysts by means of spectroscopic techniques for acetylene also different forms of adsorbed species have been reported. Both associative and dissociative acetylene adsorption can occur.

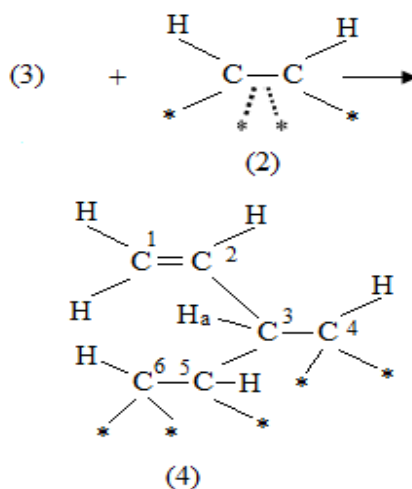
On the basis of data about carbon distribution in reaction products on Ni/SiO<sub>2</sub> catalyst. Trimm et al [15] lead his scheme of the process of oligomerization of acetylene. For its substantiation, they use data contained in studies of the catalyst surface [16] which showed that acetylene is adsorbed on the Ni centers at a temperature 120 K no dissociative and is  $\mu$ -bridging ( di- $\alpha$ / di- $\pi$  ) form. Such an intermediate suggests that the C-C bond is located across the adjacent pairs of atoms Ni - Ni and thus associated with 4 nickel atoms. The second intermediate is a vinyl group, which acts as a catalyst for connection to surface acetylene group. According to the authors, the hydrogenation of surface bonds in the third intermediate would lead to the formation of 1-butene or 1, 3-butadiene, depending on hydrogen presence on catalyst surface, and formation cis and trans-2-butene, possible if the gap of double bond is accompanied by joining of hydrogen to 1 and 4 atoms of carbon.



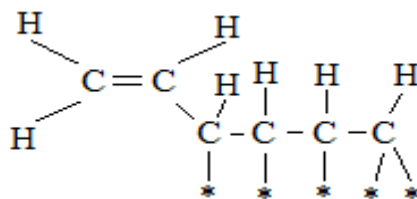
Where the symbol \* shows the connection with node of catalyst surface.

Linear hexane, hexadiene and hexatriene could be formed in the similar way if the chain extended by the addition of other surface acetylene group to the fourth carbon atom of the third intermediate.

If the surface acetylene group to join to the third intermediate, the hydrogenation of all bonds with the surface of the fourth intermediate will lead to the formation of 3-methyl-1-pentene, which was obtained in a significant quantities as a result of reaction:-

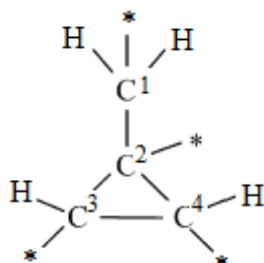


However, cis and trans-3-methyl-2-pentene, according to authors, could not be formed directly, therefore in work [15] suggested two possible ways to their formation. . The first consists that a unique diene, which could be formed directly from fourth intermediate by joining the two hydrogen atoms to the fourth carbon atom and one hydrogen atom to the sixth carbon atom was 3-methyl-1, 4-pentadiene. This is the most unstable of methylpentadiene as double bonds had not been joined; it was barely detectable in the reaction products.



In work explains that the further joining of surface acetylene group to intermediate can occur only under the condition that the resulting stresses will accumulate as many carbon atoms are for from the vinyl group and associated with the surface. As an example, the authors present linear intermediates, in which all the carbon atoms bond to the surface.

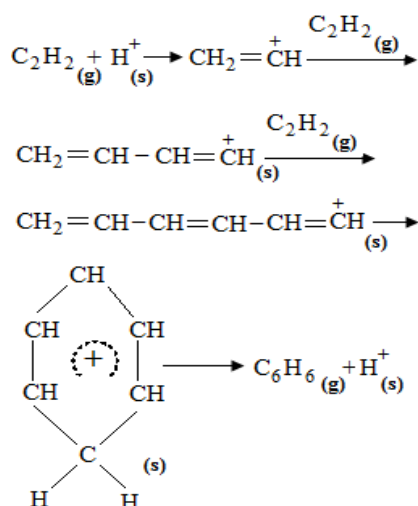
In [17, 18]the formation of 2-methyl hydrocarbons due to the formation of a transitional three-membered cyclic intermediate:



Disconnection 3-4, which is accompanied by partial hydrogenation or further increase the chain will lead to the formation of isobutylene and other 2-hydrocarbons.

The authors of work [18] offer the following general scheme of reaction on zeolite:-  
Acetylene → polyene → aromatic

Thus the data about existence of vinyl cations are presented in work [19-21]. The main reaction of the formation of benzene [18]is as follows:-



Code (s) denotes the active site of zeolite.

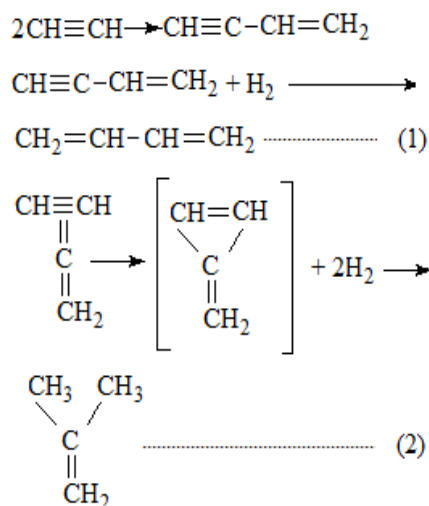
Evidence has been given that the adsorption of acetylene and ethene takes place in two stages; in the first stage an irreversible dissociative adsorption occurs, while in the second stage acetylene and ethene adsorb on this primary layer. Thus, the species that participate in the

hydrogenation reaction might not be adsorbed directly on the metal, but on a carbonaceous over layer [22-25]. It has been generally accepted that the adsorption of acetylene on Pd is much stronger than that of ethene, while ethane is adsorbed very weakly. This had led to the classical explanation for the selectivity of the acetylene /ethene hydrogenation, while in the absence of acetylene, ethene is hydrogenated readily on Pd. In this classical explanation, the selectivity was thought to be a consequence of the thermodynamic factor, which says that due to the higher adsorption enthalpy of acetylene, the ratio of surface coverages of acetylene and ethene remains very high until acetylene is virtually no longer present.

### **Mechanisms**

During the hydrogenation of acetylene in ethene, oligomers and polymers are also formed, which is a serious problem in industrial practice. These oligomers and polymers are commonly referred to as insignificant quantities from 'green oil' or liquid products; it is evident that the composition of liquid products was detected monoolefinic hydrocarbons fraction of C<sub>6</sub>-C<sub>14</sub> linear structure. Investigated the formation of green-oil and they have determined by means of gas chromatography, but received mixture of hydrocarbons was not divided by selected analytical condition, as evidenced by the imposition of the peaks on the chromatogram. Of course in the absence of acetylene no oligomers are formed. The formation of the liquid products, which remained on the catalyst surface, corresponded in their experiments to at most 2% of the consumed C<sub>2</sub>H<sub>2</sub>. The presence of these heavy polymers on the catalyst surface was examined by means of thermographic analysis, TG, and differential scanning calorimetry. From the TG experiments it was concluded that the amounts of 'heavies' was (6-36) g per kg of catalyst. The mechanisms for the oligomerization of acetylene on different catalysts. Requires knowledge of the mechanism of the reaction allows predicting and explaining the composition of the products formed and subsequently synthesizes the most effective catalysts for the process.

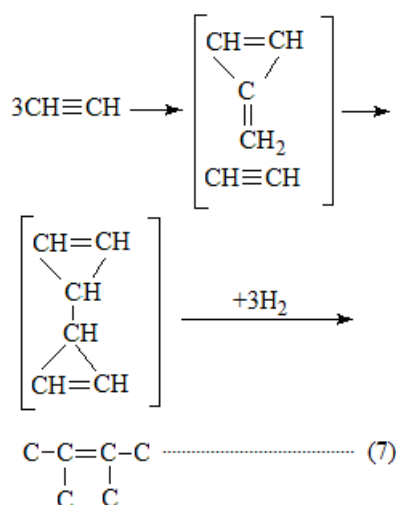
The following mechanism was presented for the dimerization of acetylene on Ni/ZnCl<sub>2</sub>/Pumice (Ni: ZnCl<sub>2</sub> = 1:5) catalyst:[26]



In [27] presented possible schemes of formation of trimers of acetylene in presence of hydrogen on Ni/Pumice catalyst.

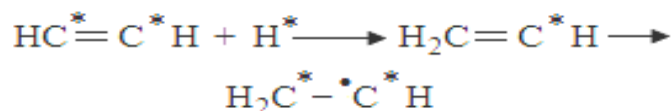
The presented schemes confirm the composition of the products obtained by this catalyst in the reaction [27] the basic trimers were 2-methyl-pentene (eq.4) ,3-methyl-pentene (eq.6)and n-hexene (eq. 3 and 5)2,3-dimethyl-butene(sidelong reaction 7)were insignificant.



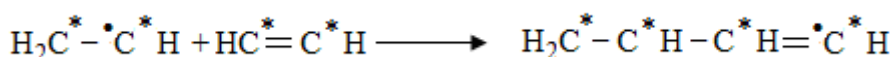


Thus, in these schemes [27] given represent formation of oligomers as a process of sequential addition of acetylene groups, and if, for linear molecules that accession can take place directly, the branched molecules are obtained through the formation and disintegration intermediate cyclopropene ring in its various relations.

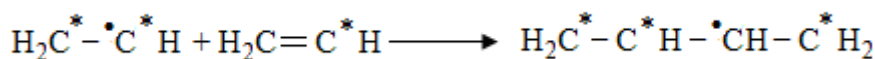
In [28] puts another original scheme of the polymerization of acetylene. This is a patter of linear and nonlinear polymerization, the so-called semihydrogenated molecules of acetylene. According to the author, the hydrogenation diadsorption acetylene molecule leads to the formation semihydrogenated structure, which can have a radical form:



Where the symbol \* shows the connection with node of catalyst surface. Accession diadsorption acetylene to the radical gives C<sub>4</sub> radical.



As a result of the further increase of a chain forms linear C<sub>6</sub> C<sub>8</sub> ... etc, reaction products.



Men'shchikov et al.[29] have performed a kinetic study of the hydrogenation of acetylene in the presence of ethene under industrially relevant conditions, using a 0.005 wt. % Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. They have found experimentally that in contrast to what previous authors had reported the rate of ethene hydrogenation is not influenced by the partial pressure of acetylene. They have considered two sets of equations, but only the two rate expressions given in equation (1) and (2) respectively, could describe their experimental data quite well over the whole experimental range of P = 2 MPa, (0.8 - 0.0002 )% acetylene, (8-0.003)% hydrogen, (0.02-1 )% ethane, 140 ppm carbon monoxide, the balance being ethene, and the temperature (353-433) K to explain the absence of an influence of the acetylene pressure on the rate of ethene hydrogenation, they put forward that acetylene and ethene might adsorb on different types of actives sites.



$$R_{C_2H_2} = \frac{K_1 K_2 K_H R_{C_2H_2} R_{H_2}}{(1 + K_2 R_{C_2H_2})(1 + K_H R_{H_2})} \dots (1)$$

$$R_{C_2H_6} = \frac{K_2 K_4 K_H R_{C_2H_4} R_{H_2}}{(1 + K_4 R_{C_2H_4})(1 + K_H R_{H_2})} \dots (2)$$

$$K_1 = 0.29 \times 10^9 \exp(-7045/T) \text{ (Kmol/sm}^3 \text{ catalyst)}$$

$$K_2 = 20.5 \times 10^9 \exp(-8050/T) \text{ (Kmol/sm}^3 \text{ catalyst)}$$

$$K_3 = 0.2 \exp(1510/T) \text{ (KPa}^{-1}\text{)}$$

$$K_H = 0.13 \times 10^{-3} \exp(1860/T) \text{ (KPa}^{-1}\text{)}$$

$$K_4 = 0.54 \times 10^{-3} \exp(1810/T) \text{ (KPa}^{-1}\text{)}$$

Thus in agreement with the later work of McGown et al. [30], and that the acetylene partial pressures applied were too low. We would like to point out that the presence of CO in their experiments might be of major importance, because if the adsorption of CO on certain type of sites is larger than that of acetylene, practically no effect of acetylene adsorption will be found. If these same sites are involved in the hydrogenation of ethene, the acetylene pressure will not influence ethene hydrogenation. Unfortunately Men'shchikov et al.[29] did not vary the CO content.

## **Experimental**

### **Preparation Pd/CNFs catalyst**

Carbon nanofibers (CNFs) were synthesized from a previous study [31] obtained also from gas electrocracking over  $\gamma\text{-Fe}_2\text{O}_3$  catalyst fig.2 (specific adsorption surface  $105 \text{ m}^2/\text{g}$  ; sorption capacity for methyl orange,  $50 \text{ mg/g}$  ; density  $2.367 \text{ g/cm}^3$  ; ash, wt 25% ; crystallite size  $280 \text{ \AA}$ ). Was prepared by incipient wetness impregnation, using aqueous solutions of palladium (II) chloride  $\text{PdCl}_2$  (99.9%, Aldrich) of appropriate concentration to obtain 0.5% (w/w) Pd. Then the catalyst dried at  $120 \text{ }^\circ\text{C}$ , and calcined it at  $400 \text{ }^\circ\text{C}$  for 5 hours. Activation of the catalyst was carried out by reduction under continuous  $\text{H}_2$  flow (300ml/min) before use. Acetylene were obtained during the decomposition of organic liquid wastes (from diesel) in an electric arc, laboratory reactor for the decomposition of organic liquid in low-voltage electrical discharges is shown in fig. 3.

The reactor is a cylindrical vessel stainless steel designed for loading of raw material in the volume of 750 ml, contains stationary graphite electrodes made in the form of parallel graphite rods, on electrodes there is a mobile intermediate contact, and between the rods there is graphite ball with a diameter  $\sim 6.5 \text{ mm}$ . When the voltage from the power supply between the stationary electrodes and a ball arc discharge occurs, this results in the decomposition of raw materials with formation of gas and soot. For reception of gas, this was used for process realizations conducted electrocracking diesel fractions. Gas composition is given in table 1.

For carried out of catalytic experiments used laboratory setup of flowing type with the integrated reactor, with the fixed bed of the catalyst (fig. 4).

Gas electrocracking was displaced from storage of gas electrocracking by water (1), after calculating the gas hourly space velocity (GHSV). Quartz reactor (6), a cylindrical (inner diameter 10 mm), with a fixed bed of catalyst, placed in the center of the electric furnace. The temperature in the catalyst bed is supported with accuracy  $\pm 20 \text{ }^\circ\text{C}$ , gaseous and liquid products of reaction leaving the reactor are cooled in the direct flow water refrigerator (8), after that condensed liquid products of synthesis, as well as water (at the stage of catalyst activation) are collected in collection (9) The other mixtures pass through a low temperature refrigerator immersed in cylindrical Dewar flask (13) for capture of light liquid hydrocarbons. The remained gaseous products pass through a glass pipette (15) (samples were withdrawn periodically and analyzed with a gas chromatograph), then a drum-type wet gasmeter (16) and released into the ventilation.

Before the beginning of carrying out of each experiment the catalyst restored by hydrogen at temperature 300 °C and flow of 25 ml/min for 2 hours, after restoration the catalyst cooled to reaction temperature in hydrogen current, then shut the gas valve of hydrogen, and recruited gas electrocracking, which is beginning to serve on the heated catalyst bed with set GHSV. After stabilizing the temperature in the catalyst bed, began to selection of samples of gas for analysis. The synthesis was carried out in the range of (GHSV) (3000-7000) h<sup>-1</sup>, and the temperature range (140-270)°C. Specific values of (GHSV) and temperature which conducted the study were chosen depending on used catalyst system. All experiments were conducted under isothermal conditions. Hydrocarbon gas analysis was performed on chromatograph mark LHM- 8. Detector - thermal conductivity detector (TCD). The current bridge detector -90 mA. Chromatographic phase - Al<sub>2</sub>O<sub>3</sub>, promoted with 5% solution of NaOH. Carrier gas flow (nitrogen) - 20 ml /min. The length of the column 7 m thermostat column - 80 °C. Analysis of liquid hydrocarbons was carried out on chromatograph Agilent Technologies gas model 6890N equipped with a mass selective detector, model 5973. Capillary column HP-1 (polymethylsyloxan), 50 m × 0.32 mm, detector temperature 280°C, injector temperature 270°C, flow rate 1.0 ml/min, initial temperature 120 °C and oven program from 5 °C/ min to 290 °C.

## **Results and discussion**

Catalyst that began to exhibit their activity at a temperature 30 °C. To investigate the effect of temperature on the stability of the catalyst compositions and reaction products, experiments were performed at (GHSV) of feed gas 4200 h<sup>-1</sup> and temperature 140 and 270 °C. It has been noted for later, that the conversion of acetylene within 6 hours of reaction in all cases was 100%. In connection with this change in catalyst activity over time was assessed by change in the conversion of hydrogen. From fig. 5, shows that over time reduces the conversion of hydrogen, especially at temperature 270 °C. Thus the increase in temperature from 140 °C to 270 °C leads to a sharp decrease in conversion. This indicates the instability of the catalyst.

Diagrams of change of the yield of the reaction products over time the process at temperature 140 °C and 270 °C are shown in fig.6 and fig.7 respectively.

From fig.6 indicates that at temperature 140 °C, one of the main products of the reaction is ethane, the yield about 44%. Yield of methane, propane is about 3.9 and 3.8%. The main products C<sub>4</sub> in the gaseous phase in the initial moment of time are butane 31.7%. However as time increase the yield of butene, which after 6 hours was 15.4% .The gradual decrease in the degree of hydrogenation of hydrocarbons C<sub>4</sub> is obviously, the reason for this change in the composition of products. It should be noted that the yield of n-butane was significantly higher yield than iso-butane yield and among the butene predominantly isobutene and 1-butene. The yield of C<sub>+5</sub> products is about 10.5%.

At temperature 270°C (fig. 7) presents that in the initial moment of time in the gas phase contains unsaturated hydrocarbons C<sub>4</sub>, their yields after 50 min. of 6.3%. With the passage of time appear in the gas phase ethene and propene, as well as yield of butene to the extent of the process.

Simultaneously the decrease in yield of the corresponding saturated hydrocarbons ethane, propane and butane. It is obvious that the proportion of the total reaction hydrogenation of hydrocarbons is decrease after 6 hours from the work of the catalyst, the yield of butene reaches 21.8%, ethene 28.9% and propene 4.9%. It should be noted that the increase in temperature from 140 °C to 270 °C leads to an increase in the yield of methane from (3.9 to 7.9) %, and decrease in the yield of C<sub>5+</sub> from (9.4 to 7.4) %. This is probably due to the fact that the temperature 270 °C there is an increase in rate of decomposition reaction of intermediates, which are precursors of hydrocarbons C<sub>5+</sub>.

The result showed high activity for palladium catalyst in hydrogenation reaction, that is obviously connected with the high maintenance of active component – palladium, as a consequence, it leads to the formation of saturated hydrocarbons C<sub>2</sub>-C<sub>4</sub> in the initial moments of time and a strong heating of the catalyst bed.

It is necessary to notice, that in all experiments, there was a decrease of catalyst activity over time. The catalyst worked unstable, thus the increase in process temperature lead to increase in the rate of its deactivation. At a temperature 240 °C the color of the catalyst became completely black, while after the experience at temperature 140 °C only insignificant dimness of granules was observed. Presents the loss of catalyst activity is connected with the deposition of carbon on its surface, the gradual blocking of the active centers of the catalyst leads to reduce the conversion of hydrogen and the reaction of partial hydrogenation. The results are in good agreement with literary data in which it is shown, that the deposition of carbon on the catalyst surface plays an important role in determining the selectivity process of hydrooligomerization of acetylene.

To study the effect of temperature on the stability of the catalyst experiments were carried out at selected temperature in (GHSV) of feed gas 4200 h<sup>-1</sup> and 6500 h<sup>-1</sup>.fig. 8, shows the change in the conversion of acetylene with time at different temperature, the reaction process and (GHSV) of feed gas 4200 h<sup>-1</sup>.

From Fig.8 shows that the stable situations of the catalyst increase with increasing temperature from 140 °C to 240 °C. At a temperature of 140 °C for 6 hours of catalyst conversion of acetylene reduced from (100 to 22) %, at temperature 200 °C for the same period of time is only reduced to 82%, and at temperature 240 °C and 270 °C full conversion of acetylene was fixed during all time of carrying out of process. Similar results of the effect of temperature have been received and at (GHSV) of feed gas 6500 h<sup>-1</sup>. It should be noted that at a temperature 140 °C on the surface of catalyst grains were found traces of liquid products (green oil).Thus suggests that the instability of the catalyst at temperatures below 270 °C is connected with the developed internal surface of the support, on which adsorption of the formed liquid products having a boiling point higher than the temperature of the experiment. As a result, the system transitions occur, subsequent reaction of adsorbed hydrocarbons that lead to the formation of high molecular component and block the active centers of the catalyst. The increase in temperature promotes evaporation of liquid products. These lead to a reduction in the rate coking and consequently increase the time stability of the catalyst.

From the fig. 9 shows increase in (GHSV) of feed gas 4200 h<sup>-1</sup> to 6500 h<sup>-1</sup> leads to a decrease in time stability of the catalyst and increase the rate of its deactivation. Because at temperature 270 °C the catalyst stably worked during time of carrying out of process in investigated area of (GHSV) is of interest to consider in detail the structure of the products at this temperature, the diagram of change in yield of the reaction products over time in the process (GHSV) of feed gas 4600 h<sup>-1</sup> shown in fig. 10.

From fig. 10 shows that the composition of the products leaving the reactor is practically dose not change within 400 min of the process. The main products are gas phase olefin hydrocarbons. Thus the yield of ethene is about 33.4%, the yield of propene 6.5%, and butene yield 22%. The yield of ethane was about 11.7%, while the yield of propane and butane were not significant and accounted for a total about 5%.

Chromatogram of liquid products, condensed under specified conditions and collected over the time of the process is shown in figure 11. It is evident that the composition of liquid products was detected monoolefinic hydrocarbons fraction of C<sub>6</sub> - C<sub>14</sub> linear structure, received mixture of hydrocarbons was not divided by selected analytical condition, as evidenced by the imposition of the peaks on the chromatogram.

As we expected, as the long term storage of liquid products in which irreversible changes connected with further transformation of unstable olefinic hydrocarbons. As a result, the refractive

index of the liquid ( $nD^{20}$ ) increased from 1.4699 to 1.4783 and for re-analysis of samples to identify the component was impossible.

The material balance of the process after 400 minutes of the catalyst at a temperature 270 °C and (GHSV) of feed gas 4200 h<sup>-1</sup> is presented in tab. 2.

Submitted material balance suggests that the hydrogenation reaction and hydrooligomerization takes only acetylene, as quantities of other hydrocarbons which are present in the feed gas, increase. It is interesting to note, that dimmers of acetylene content iso-and 1- butene was approximately two times more than the content 2-butene, and butane was present only in a linear modification.

Effect of temperature on the composition of the reaction products at (GHSV) of feed gas 4200 h<sup>-1</sup> after 120 minutes of the catalyst is shown in table 3. From tab. 3 shows that with increasing temperature from 140 °C to 180 °C there is a decrease in the yield of hydrocarbons C<sub>5+</sub> and the increase in the yield of ethane, that testifies to considerable acceleration of reaction of hydrogenation of acetylene in this interval of temperature. Further increase in temperature to 200 °C leads to decrease the yield of ethane and increase in the yield of ethene, propene and methane. It is obvious, that hydrocarbons C<sub>1</sub> and C<sub>3</sub> are formed only as a result of disintegration of less stable oligomers of acetylene.

Above 200 °C there is an increase in reaction rates of cracking. Effect of (GHSV) of feed gas on the yield of the reaction products at 240 °C is presented on fig. 11. On the graph shows the change in yield only olefinic hydrocarbons.

Apparently from fig. 12, increase in (GHSV) of feed gas from 3300 to 6300 h<sup>-1</sup> leads to a slight change in the yield of ethene and butene, in turn propene yield decrease from 8.5 to 4.5% and the yield of C<sub>5+</sub> products increased from (15.5 to 23)%. It can be assumed that with increasing (GHSV) of feed gas is an increase in the rate of desorption of intermediates formed from a catalyst surface in relation to rate of re- action of their decomposition.

As a consequence, the intermediates give rise to components of the liquid products, it should be noted that the total yield of C<sub>2</sub>-C<sub>4</sub> olefins was about 60% in an investigated interval of (GHSV), that catalyst deactivation is most possibly related with blocking its active centers by carbon deposits, and as consequence has reversible character, considered the possibility of regeneration of the catalyst.

Regeneration was carried out in hydrogen under identical restoration for one hour.

Changing the conversion of acetylene with time of the process before and after regeneration of the catalyst at a temperature 160 °C and (GHSV) of feed gas 6300 h<sup>-1</sup> is presented on fig. 13. From fig. 13 shows that after regeneration of the catalyst restores its activity, but not completely.

Regeneration catalyst works more stable than fresh; a decrease of acetylene conversion for 200 minutes of work makes 18% against 63% for the fresh catalyst.

Thus it is possible to conclude, that the main products on the catalyst 5% Pd/CNFs are indicative monoolefin hydrocarbons C<sub>2</sub>-C<sub>14</sub> predominantly linear structure. The yield of lower olefins C<sub>2</sub>-C<sub>4</sub> is more than 50%. The increase in temperature from 140 °C to 270 °C leads to an increase in time stability of the catalyst, decrease in the yield of C<sub>5+</sub> hydrocarbons and increase the yield of ethene and propene. In turn with increase in the (GHSV) of feed gas is an increase in the rate of deactivation of the catalyst. Slight change in the yield of ethene and butene, the increase in the yield of liquid products and decrease in the yield of propene.

## **Conclusions**

1. The 0.5% (w/w) Pd/CNFs catalyst has been developed appears to be very effective in the hydrogenation of acetylene, which was obtained from the gases electrocracking, and thus to the possibility of synthesis the low molecular weight C<sub>2</sub>-C<sub>4</sub> olefins, as well as hydrocarbons C<sub>5+</sub>.
2. The increase in temperature from 140 °C to 270 °C leads to a sharp decrease in conversion, this indicates the instability of the catalyst, thus the increase in process temperature lead to increase in the rate of its deactivation, the experimental results and literary data Indicate that carbon

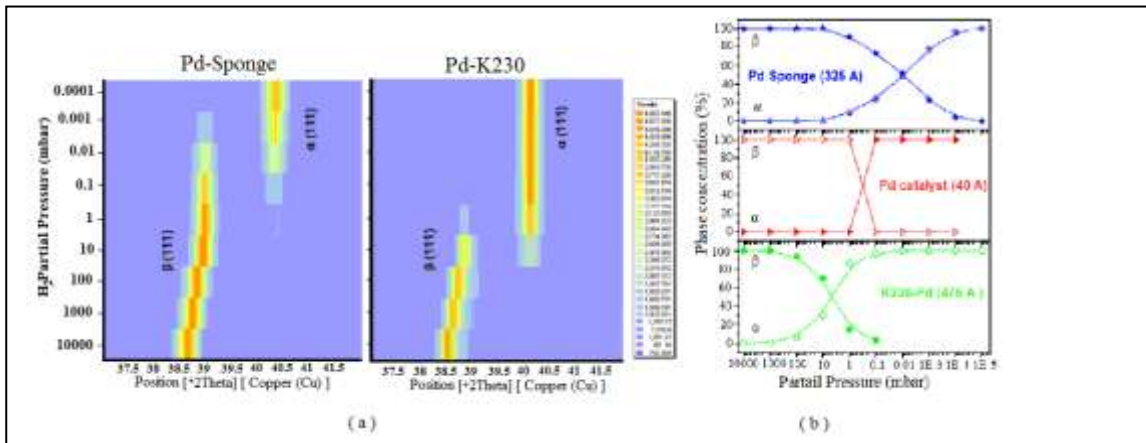
deposits on the surface of the catalyst plays an important role in determining the selectivity of hydrooligomerization of acetylene.

3. It has been shown that at low temperature and even temperature 140 °C formed traces of liquid products (green oil) , thus suggests that the instability of the catalyst at temperature below 270 °C, it was explained that the adsorption of the formed liquid products having a boiling point higher than the temperature of the experiment, it was found when increasing the temperature promotes evaporation of liquid products, these lead to a reduction in the rate coking and consequently increase the time stability of the catalyst.
4. With the gas hourly space velocity (GHSV) of feed gas from 3300 to 6300 h<sup>-1</sup>, it can be assumed that with increasing (GHSV) of feed gas leads to increased in the rate of desorption of intermediates formed from a catalyst surface in relation to rate of reaction of their decomposition.
5. The material balance of the process after 400 minutes of the catalyst at a temperature 270 °C and (GHSV) of feed gas 4200 h<sup>-1</sup> that the hydrogenation reaction and hydrooligomerization takes only acetylene, as quantities of other hydrocarbons which are present in the feed gas increasing.

## References

- [1] Toebes M. L., van Dillen J. A., de Jong K. P., J. Mol. Catal. A: Chem., **2001**, 173, 75.
- [2] Mubofu E. B., Clark J. H., Macquarrie D. J., Green Chem.,**2001**, 3, 23.
- [3] Gronnow M. J., Luque R. , Macquarrie D. J.,Clark J. H.,Green Chem.,**2005**, 7, 552.
- [4] Lee S., Park B., Byeon S.,Chang F., Kim H.,Chem. Mater,**2006**, 18, 5631.
- [5] Minkyung L., Kathlia A., Seungchan O., Kangsuk L., Young-Wook C., Hokun K., Hakjune R., Pd nanoparticles dispersed on solid supports: Synthesis, Characterization and catalytic activity on selective hydrogenation of olefins in aqueous media, Appl. Organometal. Chem.,**2011**, 25, 1-8 .Erathodiyil N., Ooi S., Seayad A. M., Han Y., Lee S. S., Ying J. Y.,Chem. Eur. J.,**2008**,14 ,3118.
- [6] Benner L. S., Suzuki L. S., Meguro T., Tanaka K., S. Precious Metals, Science and Technology, The International Precious Metals Institute, Allentown, PA,**1991**.
- [7] Augustyn W. G., McCrindle R. I., Coville N. J., J. Appl. Catal. A: General,**2010**, 388, 1-6.
- [8] Serp P., Corrias M., Klck P., Appl. Catal. A- Gen., **2003**,253, 337.
- [9] McGown W. T., Kemball C., Whan D., Hydrogenation of acetylene in excess of ethylene on a alumina supported Palladium catalyst at atmospheric pressure in a spinning basket reactor, J. Catal.,**1978**, 51, pp. 173- 184.
- [10] Bhat V. V., Contescu C. I., Gallego N. C., Payzant E. A., Rondinone A. J., Tekinalp H., Edie D. D., Proc, 2007 MRS Fall Meeting, Materials Research Society (Boston, USA).
- [11] Jain P., Fonseca D. A., Shaible E., Lueking A. E., J. Phys. Chem. C 111 , **2007**, 1788.
- [12] Bhat V. V., Contescu C. I., Gallego N. C., The role of destabilization of palladium hydride in the hydrogen uptake of Pd-containing activated carbon, (Nanotechnology 2007) ,**2009**, 20 (20), 4011.
- [13] Webb G., Hydrogenation of alkenes and alkynes and related reactions catalyzed by metals and metals complexes, Catalysis,**1979**, 2, pp. 145- 175.
- [14] Trimm D., Liu L., Cant N., Journal of Molecular Catalysis A, Chemical,**2008**, 288, pp.63- 74.
- [15] Medlin J. W., Allendorf M. D., J. Phys. Chem. B, **2003**, 107, 217.
- [16] Kenneth N. C., Barbara K. C., The addition of hydrogen to multiple carbon-carbon bonds, Chem. Rev., **1942**,31(1), 77- 175.
- [17] Tsai P., Anderson J. R., J. Catal., **1983**, 80, pp.207- 214.
- [18] Deno N. C., Carbonium Ions, Wiley-Interscience, New York, 1970, pp. 783.
- [19] Richey H. G., Richey J. M., Carbonium Ions, Wiley-Interscience, New York, 1970, pp. 899.
- [20] Stang P. J., Rappoport Z., Hanack M., Subramanian L. R., Vinyl Cations, Academic Press, New York , 1979.
- [21] New York , 1979.

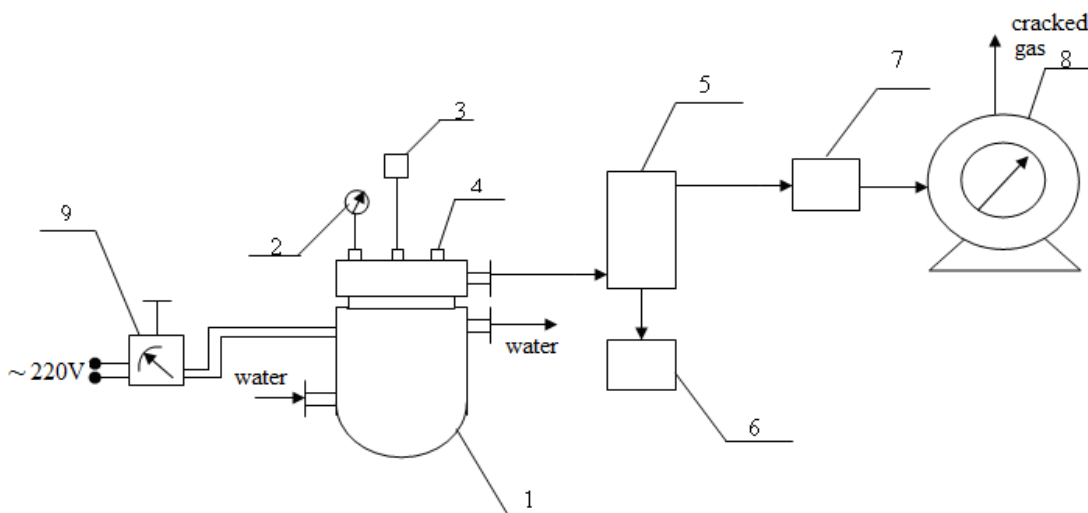
- [22] Al-Ammar A. S., Webb G., Hydrogenation of acetylene over supported metal Catalysts, part 2, J. Chem. Soc., Faraday Trans.1, **1978**, 74 , pp.657- 664.
- [23] Al-Ammar A. S., Webb G., Hydrogenation of acetylene over supported metal Catalysts, part 1, J. Chem. Soc., Faraday Trans. 1,**1978**, 74, pp. 195- 205.
- [24] Al-Ammar A. S., Webb G., Hydrogenation of acetylene over supported metal Catalysts, part 3, J. Chem. Soc., Faraday Trans. 1, **1979**, 75, pp.1900-1911.
- [25] Margitfalvi J., Gucci L., Weiss A. H., Reactions of acetylene during hydrogenation on Pd black catalyst, J. Catal., **1981**, 72, pp. 185- 198.
- [26] Sheridan J., The metal-catalysed reaction between acetylene and hydrogen. Part II. Further experiment with nickel catalysts, J. Chem. Soc., **1945**, 133- 142.
- [27] Antsus L. I., Petrov A. D., Ed. Russian Academy of Sciences, Chem. Sci., **1942**, 2 (3), 125.
- [28] Sheridan J., J. Chem. Soc., **1945**, 133.
- [29] Bos A. N. R., Westerterp K. R., Mechanism and kinetics of the selective hydrogenation of ethyne and ethane, Chem. Eng. Proc. Process Intensification, **1993**, 32(1), 1-7.
- [30] McGown W. T., Kemball C., Whan D., Hydrogenation of acetylene in excess of ethylene on a alumina supported palladium catalyst at atmospheric pressure in a spinning basket reactor, J. Catal., **1978**, 51, pp. 173- 184.
- [31] Nikolaev A. I., Peshnev B. V., Ismail A. S., Production of carbon nanofibers from the gas electrocracking on iron oxide catalyst, Solid Fuel Chemistry J., **2009** ,4(1), 35- 37.



**Figure 1:** (a) XRD patterns of Pd-sponge and Pd-ACF under different hydrogen partial pressures; (b) degree of  $\beta \rightarrow \alpha$  conversion of Pd hydride phases as a function of H<sub>2</sub> pressure. [11]



**Figure 2:** SEM images of the CNFs obtained by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst at 400 °C, and (GHSV) 1600 h<sup>-1</sup>



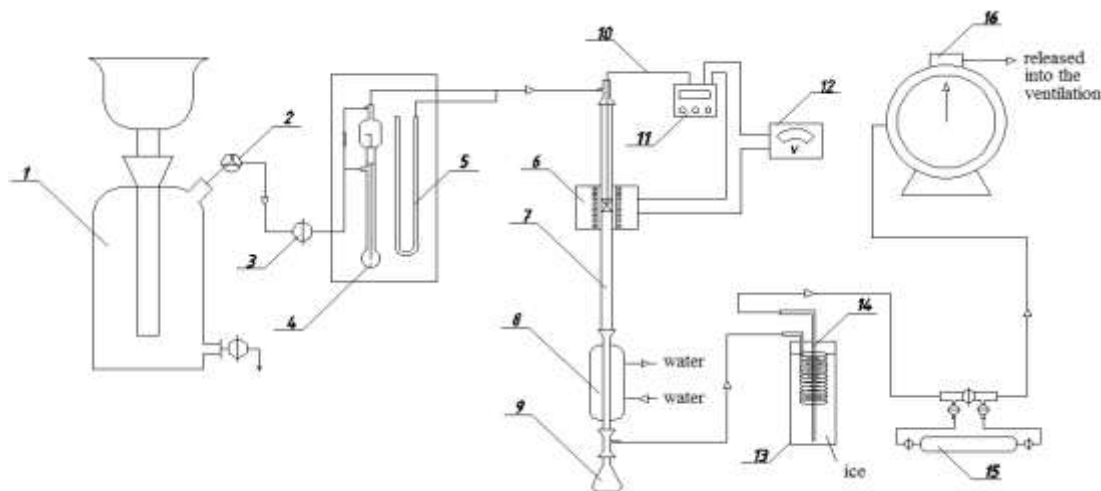
**Figure 3.**Schematic diagram of the laboratory setup gas electrocracking organic materials

- |   |  |
|---|--|
| <ul style="list-style-type: none"> <li>1. Reactor stainless steel.</li> <li>2. Monometer.</li> <li>3. Thermoregulatory-controller PID- OWEN-TRM 12.</li> <li>4. Fitting for a fill raw material.</li> <li>5. Filter.</li> </ul> | <ul style="list-style-type: none"> <li>6. Bunker for filtered soot.</li> <li>7. Location for withdrawn gas electrocracking for analysis.</li> <li>8. Drum-type wet gasmeter.</li> <li>9. Laboratory transformer of a current.</li> </ul> |
|---|--|

**Table 1. Composition of gas electrocracking diesel fraction**

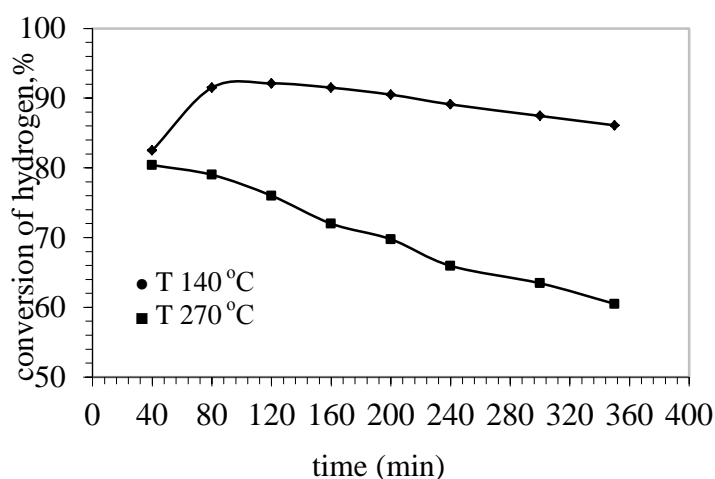
component	% vol.
H <sub>2</sub>	61-64
CH <sub>4</sub>	2.5-3
C <sub>2</sub> H <sub>6</sub>	0.4-0.7
C <sub>2</sub> H <sub>4</sub>	5-6
C <sub>3</sub> H <sub>6</sub>	0.8-1.5
C <sub>2</sub> H <sub>2</sub>	27-29



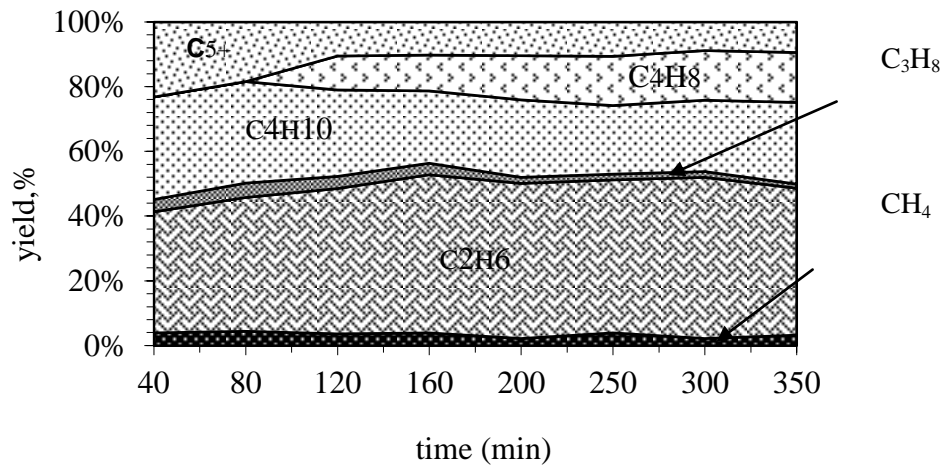


**Figure 4.** Schematic diagram of the laboratory setup of this study

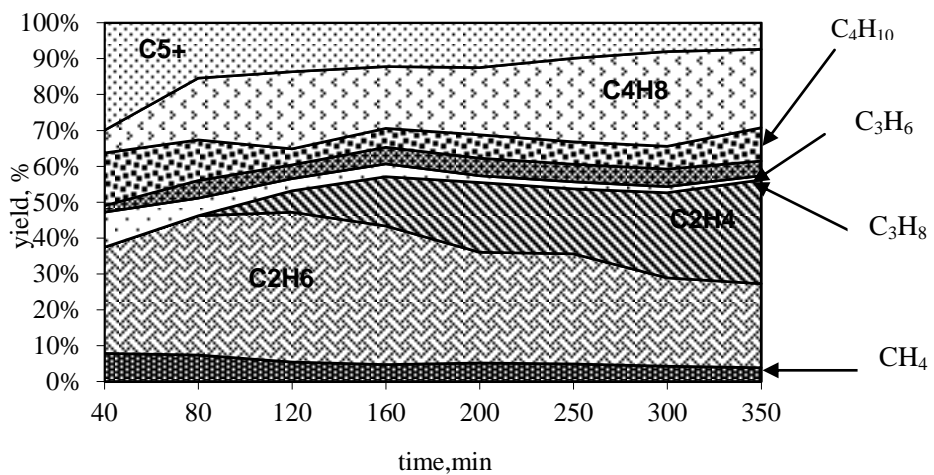
- |  |  |  |
|--|--|--|
| 1. Storage and pumping of gas electrocracking. | 7. Quartz reactor.                               | 12. Laboratory transformer of a current. |
| 2. Three- way valve.                           | 8. Water refrigerator.                           | 13. Cylindrical Dewar flask.             |
| 3. Valve adjustment of feeding gas.            | 9. The collection of liquid products.            | 14. Low-temperature refrigeration.       |
| 4. Rheometer.                                  | 10. Thermocouple wire-type k (Chromel-Alumel).   | 15. Pipette for gas samples.             |
| 5. U-shaped tube –pressure monometer.          | 11. Thermoregulatory-controller PID-OWEN-TRM 12. | 16. Drum-type wet gas meter.             |
| 6. The electric furnace.                       |  |  |



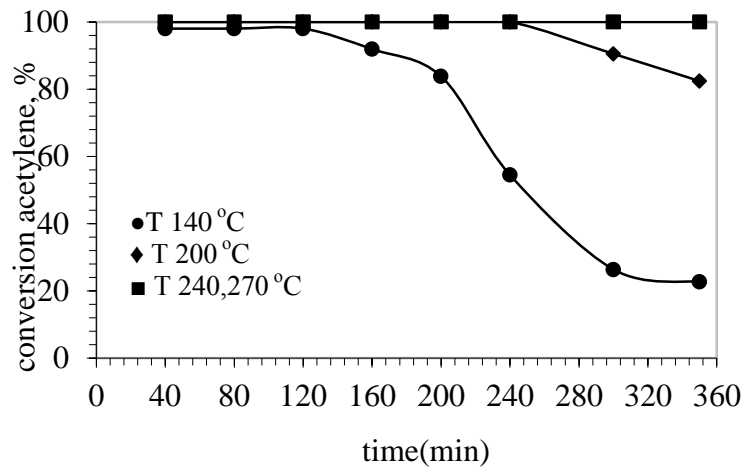
**Figure 5.** Dependence of the conversion of hydrogen from the time of the process at different temperatures, (GHSV) of feed gas 4200 h<sup>-1</sup>



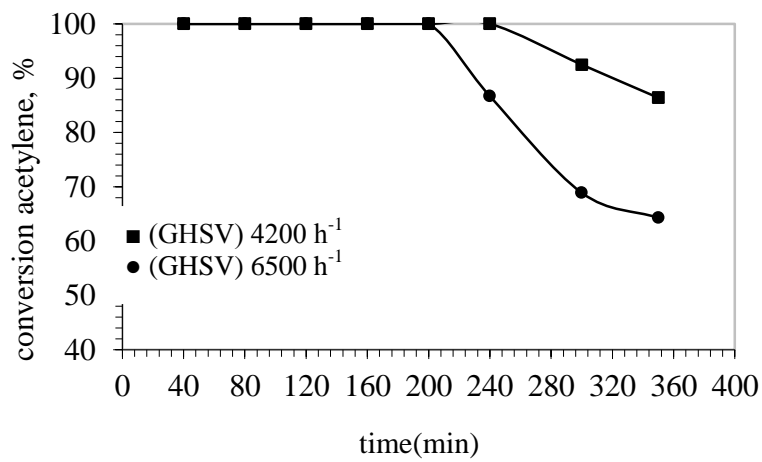
**Figure 6.** Change in the yield of the reaction products with time at a temperature of 140 °C and (GHSV) of feed gas 4200 h<sup>-1</sup>



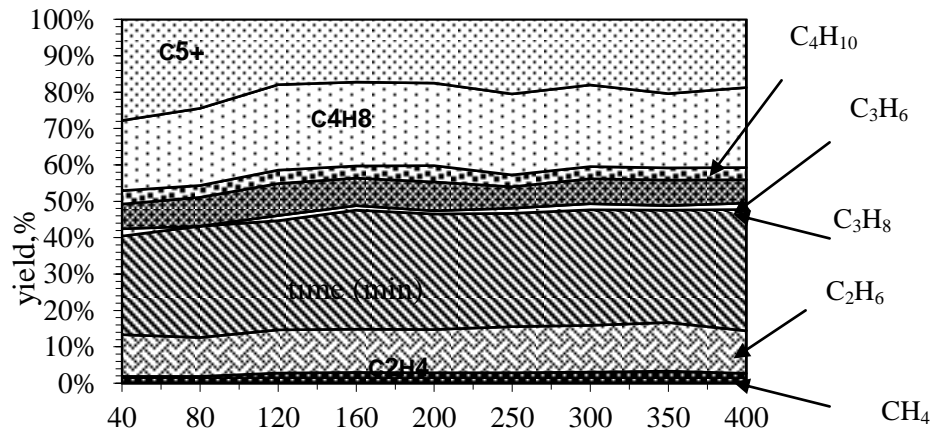
**Figure 7.** Change in the yield of the reaction products with time at a temperature of 270 °C and (GHSV) of feed gas 4200 h<sup>-1</sup>



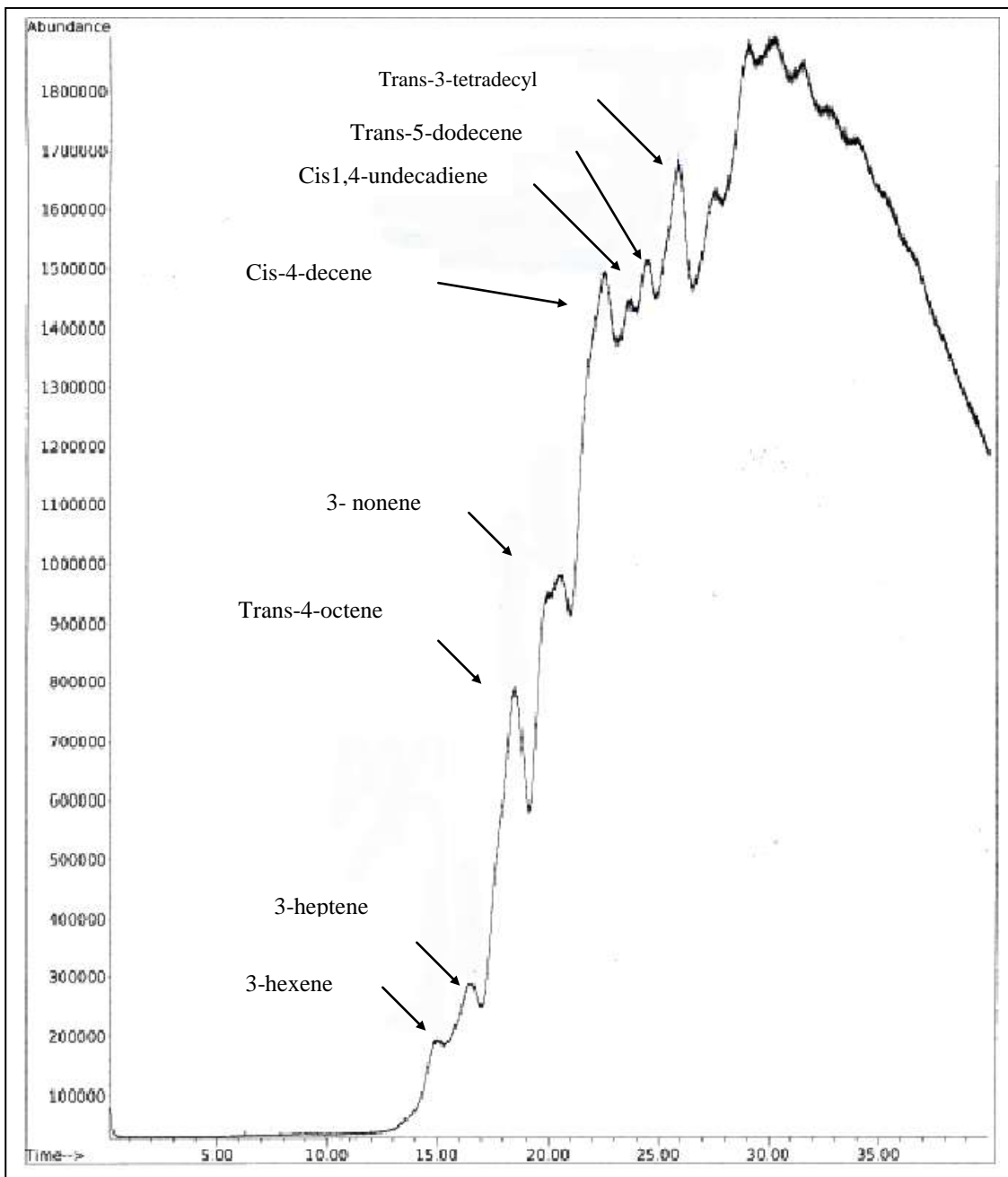
**Figure 8.** Dependence of the conversion of acetylene on time of process at different temperatures,(GHSV) of feed gas  $4200 \text{ h}^{-1}$



**Figure 9.** Dependence of the conversion of acetylene on time of process at different (GHSV) of feed gas, at temperature  $200 \text{ }^\circ\text{C}$



**Figure 10.** Change in the yield of the reaction products with time at a temperature 270 °C and (GHSV) of feed gas 4600 h<sup>-1</sup>



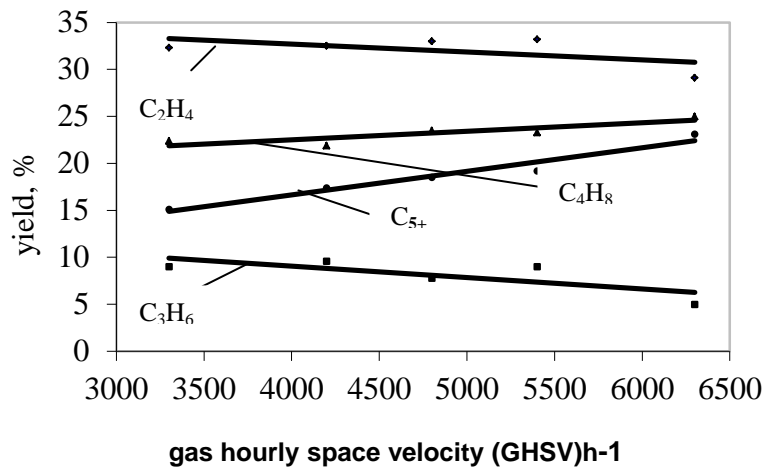
**Figure 11.** Chromatogram of liquid products, collected over 400 minutes of process, temperature 270 °C and (GHSV) of feed gas 4200 h<sup>-1</sup>

**Table 2. Material balance of process (t=400 min, T=270 °C , w=4200 h<sup>-1</sup>)**

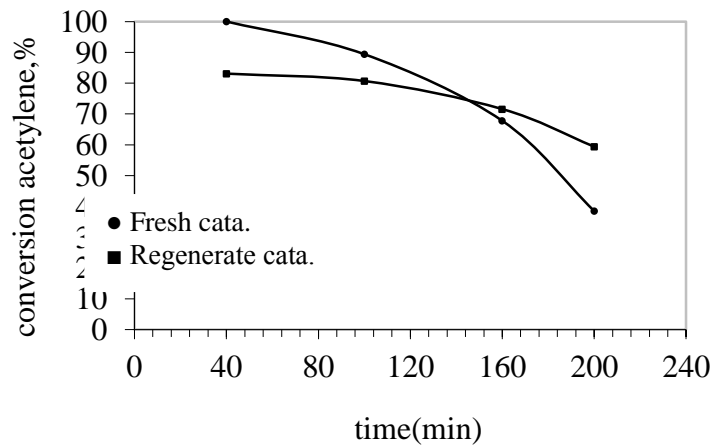
Incoming			Outgoing		
Contents/gas	% vol.	% mass	Contents/gas	% vol.	% mass
H <sub>2</sub>	61.2	10.8	H <sub>2</sub>	47.1	4.7
CH <sub>4</sub>	2.5	3.5	CH <sub>4</sub>	7.2	5.7
C <sub>2</sub> H <sub>4</sub>	5.3	13.0	C <sub>2</sub> H <sub>6</sub>	7.3	10.8
C <sub>2</sub> H <sub>2</sub>	29.2	66.8	C <sub>2</sub> H <sub>4</sub>	27.3	37.8
C <sub>2</sub> H <sub>6</sub>	0.7	1.8	C <sub>3</sub> H <sub>6</sub>	4.2	8.7
C <sub>3</sub> H <sub>6</sub>	1.1	4.1	(i+a)- C <sub>4</sub> H <sub>8</sub>	3.8	10.5
In total	100.0	100.0	β- C <sub>4</sub> H <sub>8</sub>	1.9	5.3
			n- C <sub>4</sub> H <sub>10</sub>	0.6	1.7
			C <sub>3</sub> H <sub>8</sub>	0.6	1.3
			∑ C <sub>5+</sub>		13.5
			In total	100.0	100.0

**Table 3 .Effect of temperature on the yield of the reaction products (w=4200 h<sup>-1</sup>, t=120 min)**

Temperature , °C	conversio n C <sub>2</sub> H <sub>2</sub> , %	yield, %							
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	∑C <sub>4</sub> H <sub>8</sub>	n-C <sub>4</sub> H <sub>10</sub>	C <sub>5+</sub>
140	100	1,6	13,4	27,7	1,5	6,2	21,9	2,8	24,7
180	100	2,3	19,4	28,0	1,4	5,8	23,1	3,1	16,9
200	100	2,8	11,9	31,0	1,4	8,8	23,5	2,7	17,9
240	100	4,2	10,8	32,1	2,1	8,3	22,0	2,0	18,6



**Figure 12.** Dependence of yield of reaction products on (GHSV) of feed gas, temperature 240 °C



**Figure13.** Dependence of the conversion of acetylene on the time of the fresh and regenerated catalyst, temperature 160 °C, (GHSV) of feed gas 6300 h<sup>-1</sup>