

Hydrooligomerization of Acetylene from Electrocracking Gas over Ni/CNFs Catalyst

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Abstract: Carbon nanofibers (CNFs) supported nickel catalysts (Ni/CNFs) for hydrogenation of hydrocarbons were prepared by a slurry type impregnation procedure method for the reaction of electrocracking gas in the presence of acetylene and hydrogen in a flow system are investigated. Samples containing 5.0 wt% Ni are capable of complete acetylene conversion over a period of 5 h at 170 °C when using a 27-29% C₂H₂ and 61-64% H₂ from the percentage of composition of electrocracking gas diesel fraction feedstocks. The amount of ethane and ethylene equivalent to approximately half of acetylene converted with propane, propylene and methane formation low, As well as the remaining percentages of acetylene converted into higher hydrocarbons through hydrooligomerization. Predominant product distributions are linear alkenes (C₄+ - C₅+) followed by branched alkenes (isobutene and isopentene), traces of dienes. Other products, that appear are liquid hydrocarbons or (green oils). Catalytic experiments were performed in a fixed bed reactor at atmospheric pressure, using gas hourly space velocity (GHSV) in 5920 h⁻¹ (30 ml/min) of feedstock gas.

Keywords: catalysts (Ni/CNFs), electrocracking gas, hydrooligomerization, gas hourly space velocity .

Introduction

The advent of nanostructured support materials such as ordered mesoporous materials, [1] carbon nanofibers, [2-5] and carbon nanotubes [6, 7] provides opportunities for novel supported metal and metal oxide catalysts. Carbon nanofibers and carbon nanotubes are promising support materials in view of, among others, the control of surface properties, chemical inertness, the high accessibility, thermal stability, mechanical strength, and tunable bulk density. The field of carbon nanofiber supports has been pioneered by the groups of Baker,[8,9] Geus,[10] Ledoux, [11] and De Jong. [12,13] Recently, Serp and co-workers [14] have written a review on the status of the use of carbon nanofibers (CNF) and carbon nanotubes (CNT) as support material. Compared to activated carbons, CNFs offer high specific surface area due to meso-pores without micro-porosity, thus preventing internal both paraffins and aromatics over nickel diffusion limitations. In addition, their graphitic structure leads to specific metal– support interactions, which improves the catalytic activity/ selectivity. Thus, CNF supports have been reported to induce an increase in the catalytic performance of nickel nanoparticles during hydrogenations of 1-butene, 1,3-butadiene [15] Other reports have shown advantageous properties of CNFs catalytic supports

[16-18]. The required catalysts must be capable of hydrogenating small concentrations of alkynes in the presence of large amount of alkenes [19-24]. The high selectivity presumably resides in differences in adsorption strength of the unsaturated molecules or/and subsequent surface reaction kinetics [25, 26]. Acetylene produced or cobalt supported on ZSM5 zeolite-alumina, in the presence of steam at 350°C [27, 28]. On nickel–chrome wire, acetylene yielded several aromatic hydrocarbons, mainly benzene at 550 – 650 °C [29]. Acetylene adsorption was studied on Ni (111) [30] and several species were found among them adsorbed benzene. Recently, alumina supported nickel was found to be very selective to ethylene in acetylene hydrogenation [31]. From the above literature data, fundamental studies on selective acetylene hydrogenation on nickel catalysts appear as rather rare up to now [27-30]. Moreover, on nickel catalysts, it has been shown that acetylene aromatization occurs only at high reaction temperature, around 300–650 °C [27, 28, 32].

In this paper we will focus on the use of carbon nanofibers as support material while using wet impregnation method, for the preparation of supported nickel catalysts. Nickel-based catalysts are widely used in processes such as hydrogenations, steam reforming, amination, and hydrodesulphurization.

Experimental

Catalyst preparation: Carbon nanofibers (CNFs) were synthesized from a previous study [33] obtained also from electrocracking gas diesel fraction feedstocks over $\gamma\text{-Fe}_2\text{O}_3$ catalyst figure 1 (specific adsorption surface 105 m²/g ; sorption capacity for methyl orange, 50 mg/g ; density 2.367 g/cm³ ; ash, wt 25% ; crystallite size 280Å). From (~7 gm) carbon nanofibers, is then treatment carbon nanofibers that has been prepared using $\gamma\text{-Fe}_2\text{O}_3$ catalyst, in order to remove the remains of small quantities of iron are present in carbon nanofibers by refluxing 1M KOH solution for 2 h. The remaining carbon nanofibers were refluxed in a mixture of concentrated nitric acid and sulfuric acid (1:1) for 30 min. This results in removal of the accessible iron originating from the growth catalyst and surface oxidation of the carbon nanofibers. After being thoroughly washed, the carbon nanofibers were dried overnight at 120°C.

CNF-supported Ni catalyst was prepared by a slurry type impregnation procedure using Nickel (II) nitrate hexahydrate (99.999% pure [Ni (NO₃)₂.6H₂O] obtained from Sigma- Aldrich) as a nickel source with 5.0% Ni weight as precursor, was added of the supported by drying at 100 °C for 4 h, and then calcined at 450 °C for 2 h and reduced in a flowing H₂ - N₂ mixture at 250 °C for 1 h. The as-obtained catalyst was designated as Ni/CNFs.

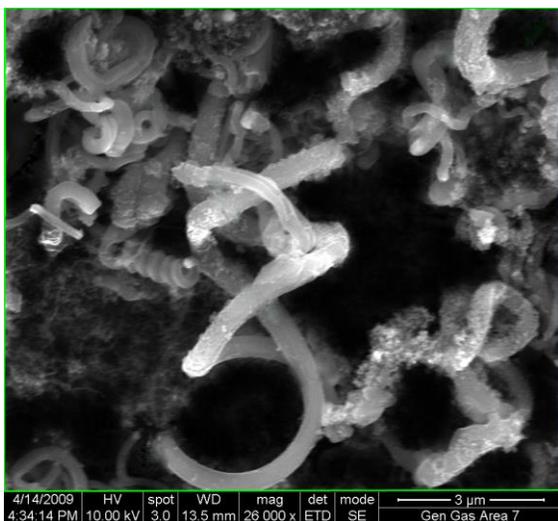


Figure 1: SEM images of the CNFs obtained by $\gamma\text{-Fe}_2\text{O}_3$ catalyst at 400 °C, and (GHSV) 2500 h⁻¹

Catalyst characterization:The Ni content in catalyst was analyzed using inductively coupled plasma emission spectrometry, sequential

spectrometer (ICP-OES, 2000TMDV Perkin-Elmer, Shelton, CT, USA). A CNF, like other carbon structured materials (e.g., graphite), is very difficult to bring into solution by conventional acid wet digestion due to its stable composition. Some works have used a dry ashing method for digestion of CNT (550 °C by 3 h) and further analysis by inductively coupled plasma mass spectrometry ICPMS [34]. Strong et al [35] performed the determination of metal impurities in CNTs by ICPMS after partial digestion using aqua regia. However, as the digestion was incomplete, the undissolved fraction must be analyzed by XRF. Underestimated results were found for some metals, and it was suggested that a shell carbon surrounded the metal catalyst avoiding an efficient attack by aqua regia. Plasma operating conditions and wavelength used for Ni determination are listed in table 1.

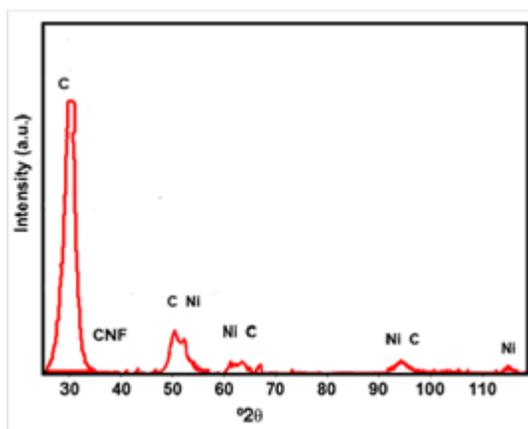


Figure 2: X-ray diffraction pattern of Ni/CNFs catalyst

Table 1: Operational parameters for ICP OES determination

ICP OES Settings	
power (W)	1400
RF generator (MHz)	27
Ar plasma flow rate (L min ⁻¹)	12
Ar auxiliary flow rate (L min ⁻¹)	1.0
Ar nebulizer flow rate (L min ⁻¹)	1.0
spray chamber	Scott double pass
Nebulizer	cross flow
Analytical Wavelength (nm)	
Ni	231.601

The XRD patterns were recorded with X-ray diffraction diffractometer (Rigaku D/MAX-2400, equipped with graphite monochromatized Cu K α radiation, in the 2 θ ranges from 20 to 110 in a 2 θ system, from the XRD patterns (Figure 2), wide diffraction peaks of Ni particles can be seen. A broad and intense diffraction line close to 30° 2 theta and weaker lines at 50°, 62° and 95° reveal the graphite-like character of the CNF materials. With the CNFs the presence of metallic nickel is apparent from the XRD pattern. The analyses were achieved in Lomonosov Moscow University of Fine Chemical Technology.

Catalytic activity measurement

The catalyst was stabilized for 5 hours at temperature 170 °C, survey experiments were also carried out at temperatures 150 to 240°C, under the reaction conditions by passing the electrocracking gas for diesel fraction, depending on the ratio of volumetric to each of the hydrogen and acetylene gas, which is equal to (62.5, 28 % vol.) respectively, at gas hourly space velocity (GHSV) 5920 h⁻¹ (30 ml/min) and carried out in the other (GHSV), and charged with carbon nanofibers (CNFs) (0.5g) as supported and the catalyst 5%Ni, survey experiments were also carried out with different Ni loadings. The reaction lasted for 300 min without regeneration and after regeneration. All preparations were dried at 100 °C for 4h and calcined at 450 °C for 2h. Individual samples were loaded into the reactor and reduced in pure H₂-N₂ mixture (to 250 °C, hold for 1 h). Experiments were performed with atmospheric pressure. Most of the experiments were performed using a chromatograph mark LHM- 8.

Catalyst tests

Acetylene was obtained during the decomposition of organic liquid wastes (from diesel oil waste) in an electric arc. 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 ~6.5 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 2.

Table 2 : Composition of electrocracking gas diesel fraction

Component	% vol.
H ₂	61-64
CH ₄	2.5-3
C ₂ H ₆	0.4-0.7
C ₂ H ₄	5-6
C ₃ H ₆	0.8-1.5
C ₂ H ₂	27-29

For carried out of catalytic experiments used laboratory setup of flowing type with the integrated reactor, with the fixed bed of the catalyst, after calculating the gas hourly space velocity (GHSV). Quartz reactor, 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 ± 5 °C, gaseous and liquid products of reaction leaving the reactor are cooled in the direct flow water refrigerator, after that condensed liquid products of synthesis, as well as water (at the stage of catalyst activation) are collected in collection. The other mixtures pass through a low temperature refrigerator immersed in cylindrical Dewar flask for capture of light liquid hydrocarbons. The remained gaseous products pass through a glass pipette (samples were withdrawn periodically and analyzed with a gas chromatograph), then a drum-type k wet gasmeter, and released into the ventilation.

Before the beginning of carrying out of each experiment the catalyst restored by H₂-N₂ mixture at 250 °C and flow of 25 ml/min for 1 hours, after restoration the catalyst cooled to reaction temperature in hydrogen current, then shut the gas valve of hydrogen, and recruited electrocracking gas, 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. 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 - Al₂O₃, 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 (polymethylsiloxan), 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.

Conversion efficiency and catalyst longevity

As is usual for Fischer -Tropsch type system, the catalysts were made with a high metal content in order to maximize activity and minimise the fraction that was difficult to reduce through formation of metal/carbon nanofibers. The variations of product distributions with changes in the %Ni atom loading on carbon nanofibers (CNFs) support in the electrocracking gas reaction are shown in figure 3 and table 3. All runs were carried out at 170 °C and product distributions shown are those obtained for only one hour on stream conversion at a gas electrocracking in gas hourly space velocity (GHSV) of 5920 h⁻¹ (30 ml/min).

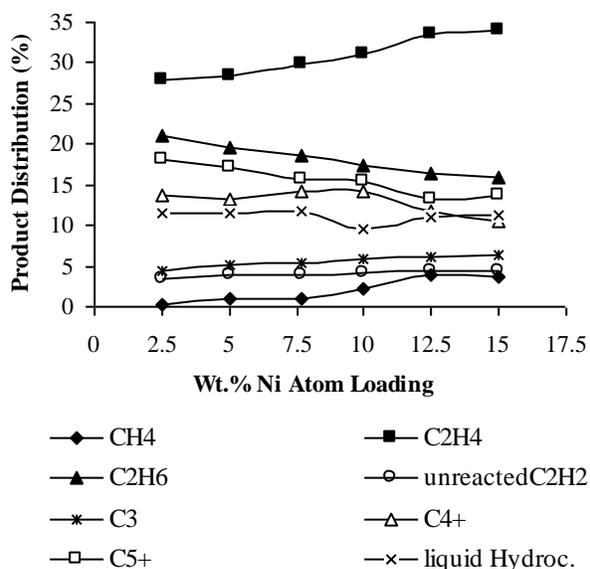


Figure 3: Effect of variation of nickel atom loading of the catalyst on the product distribution for reaction of gas electrocracking

In all experiments, the amount of ethylene increased with time on stream, at about a similar rate as ethane production was low. The main products in the gas phase in the initial moments of stream are ethylene and ethane, general, similar product distributions were observed at the time of deactivation (in other words, the first appearance of unreacted acetylene) for all Ni atom loading. It should be noted that the analysis of the liquid hydrocarbons showed a broad variety of olefins (3-hexene, 3-heptene, trans-4-octene, 3-nonene, cis-4-decene, cis 1,4-undecadiene,

trans-5- dodecene and trans-3-tetradecyl), with very little paraffins. Their relative concentrations decreased as the molecular weight increased, with other larger amounts of even numbered carbon compounds being observed. About 24-31% of the C₄₊ and C₅₊ fractions were C₆ hydrocarbons, this is probably due to the fact that at 170 °C is an increase in the decay rates of reaction intermediates that are precursors of C₄₊ and C₅₊ hydrocarbons.

Surprisingly, it was observed that the catalyst longevity was not increased with increasing Ni loading. In fact, shorter catalytic lifetimes were noted at higher Ni loading, as shown in table 4. The deactivation times listed indicate when unreacted acetylene is first detected in the product stream. In which catalytic stability required a minimal loading of nickel and improved with higher Ni content. In the present study, the variation in Ni atom loading appears to have relatively little influence on the hydrooligomerization reaction, as shown by the relative constancy of the C₄₊ and C₅₊ fractions in figure 3. This may indicate that polymerization reactions occur on the catalyst support, with relatively little influence being exerted by the nickel atoms on the polymerization reaction. Moreover, the extent of nickel loading increases hydrogen consumption which implies more coke formation. In addition to the above analysis, observations on the physical properties of the catalysts with changing Ni atom loading may be relevant in terms of decreased catalytic lifetime at higher Ni loading. It was noted that both the hardness and the bulk density of the final catalyst product increased as the percentage of nickel was increased.

In light of the data obtained, 5 % nickel loading was chosen for further studies. This decision was based on two factors: first, the increased Ni loading may severely affect the dispersion size of the Ni atom cluster on the catalyst, and second, it was observed that 5% nickel catalyst provided the most stable product distribution with time on stream. Figure 4 shows the data obtained from the components of the raw electrocracking gas, which resulted from the cracking diesel oil waste, using electric arc and product distributions in electrocracking gas conversions for reactions carried out at fixed Ni atom loading (5%). Product distributions of hydrocarbons shown are those obtained after 1hour of time on stream and at 170 °C.

From figure 4 shows the product distributions obtained for reactions of electrocracking gas containing a fixed ratio of H₂/ C₂H₂, which is equal to 2.23 : 1 and this ratio provided stable product distributions for prolonged reaction periods, it was

successfully achieved for over 5 hours using Ni/CNFs catalyst. A 5 % Ni on CNFs support was found to provide optimum catalyst activity, and continuous conversion of hydrogen/acetylene to other hydrocarbons, after the complete hydrogenation and hydroooligomerization reactions, and increased the proportion of hydrocarbons, that were originally found in a gas electrocracking, previously described in the table 2 , which included methane, ethylene, ethane, propylene and propane, in addition to new products such as C4+ and C5+ fractions and liquid hydrocarbons , as well as it appears in table 2 and 3, the deactivation times listed indicate when un reacted acetylene is first detected in the product stream.

Variation of Conversion Temperature

The effect of conversion temperature on product distributions and catalytic lifetime were carried out, also the catalyst employed consisted of 5%Ni. Figure 5 shows that the reduction of C₂H₂ to C₂H₆ is more efficient at lowest temperature 150 °C. This is probably because of the exothermic character of this reduction reaction. As noted earlier, catalytic deactivation with time on stream can generally be noted by a decrease in C₂H₆ formation. It should be noted that at 150 °C, and less this temperature, in the grain surface of the catalyst was found traces of liquid products. This suggests that the instability of the catalyst at temperature below the 170 °C, and associated with nature of the internal surface of the catalyst in which adsorption of liquid products having a boiling point higher than the temperature of the experiment. At 170 °C the catalyst deactivated in 5 hours. This catalytic can be attributed to the formation of high boiling point oligomers, which may condense on the catalyst. However, no improvement in the catalyst lifetime was obtained at temperatures above 240 °C. Presumably, the consecutive reactions lead to the formation of high molecular compounds and block the active sites of the catalyst, and increasing the temperature to evaporate liquid products formed, which leads to a decrease in coking rate.

Overall, these results are indicative of an optimal temperature for this conversion process. Table 5 shows the corresponding data from for effect of variations of conversion temperature on the relative product distributions.

Variation of Conversion Time

Figure 6 shows the product distribution as a function of time, the product distribution became relatively stable with prolonged time on stream. However, there was a slow progressive and downward variation in product yield with time on stream, most notably a slow decrease in C5+ and ethane yields accompanied by increasing of ethylene and a slight increase in C4+. It was observed that the total peak area in GC analysis decreased significantly with time on stream. The reduction in the total GC area was an indication that higher molecular weight compounds were

formed. These higher molecular weight compounds remained in the reactor and in the collection of liquid products, leading eventually to blockage of the product flow, and remained percentage of ethylene and C4+ as a product of the oligomerization and hydrogenation processes. In other words, higher amounts of C4+, C5+ hydrocarbons do not necessarily mean more polymerization. A decrease in C5+ concentration might indicate that more carbon atoms have been used to make heavier oils that remain in the reactor and in the collection of liquid products, with subsequent decrease in the GC total peak area.

The oligomerization process was proposed to occur on the carbon nanofibers (CNFs). This result indicates that Ni/CNFs catalyst is a bifunctional, where the carbon nanofibers (CNFs) act not only as a metal support but also actively participates in acetylene conversion.

Analysis of heavy liquid products collected from the collection of liquid products showed abroad variety of paraffins and olefinic compounds. Absence of aromatics has also been reported in the green oil formed during the selective hydrogenation of acetylene in ethylene stream with Pd/CNFs catalyst [36].

Variation of Gas Hourly Space Velocity (GHSV)

Effect of gas hourly space velocity for feedstock electrocracking gas on the yield of product distribution at 170 °C is shown in Figure 7. As can be seen from figure increase in the gas hourly space velocity from 4920h⁻¹ (20ml/min) to 14760 h⁻¹ (60ml/min) leads to a slight change in yield ethane and ethylene, thus for a yield other hydrocarbons, as methane, propylene and propane, higher GHSV might not provide sufficient time for the reactants and/or products to diffuse throughout the carbon nanofibers (CNFs) pores, acetylene molecules that are not able to get into the pores during the first stages of the catalytic bed might react on the surface of the particle. These unprotected reactions may polymerize on the catalyst surface thereby blocking the catalyst's entrance into the carbon nanofibers (CNFs) pores leading to eventual catalyst deactivation

While C₄₊ and C₅₊ products increased from 3.0 to 6% when increase the gas hourly space velocity for feedstock electrocracking gas from 4920 h⁻¹ to 14760 h⁻¹. It can be assumed that an increase in the gas hourly space velocity for feedstock electrocracking gas is an increase in the rate of desorption of intermediates formed on the catalyst surface with respect to the reaction rate of decay. As a consequence, intermediates give rise to components of the liquid products.

Based on the fact that the deactivation of the catalyst is most likely related to the blocking of its active sites of carbon deposition and consequently, is reversible, has been considered the possibility of regeneration of the catalyst.

The continuous conversion of acetylene, which was obtained from the electrocracking gases, and thus to the possibility of synthesis the low molecular weight C_{4+} - C_{5+} fractions as well as other hydrocarbons was successfully achieved for 300 minutes, and using Ni/CNFs catalyst. A 5%Ni on carbon nanofibers (CNFs) support was found to provide optimum catalyst activity. Higher nickel loading increased the formation of CH_4 , C_2H_6 and C_3H_8 , resulted in more rapid catalyst deactivation. Conversion temperature studies indicated that 170 °C seems to be the optimum conversion temperature under the above reaction conditions. At higher temperature the catalyst was rapidly deactivated, and lower temperature, less heavy liquid products (green oils) were collected from the reaction. 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, although the desired reduction process was increased at lower temperatures. Conversion resulted in condensation and retention of heavier oligomers in the catalyst. At a give gas hourly space velocity (GHSV) of feedstock from 5920 to 14760 h^{-1} , catalyst lifetimes were observed to be very dependent on the absolute reactant feedstock rate. This was also attributed to diffusion limitation in the catalyst. Although progressive increase in fraction C_{4+} , it can be assumed that with increasing (GHSV) of feed gas leads to increase in the rate of desorption of intermediates formed from a catalyst surface in relation to rate of reaction of their decomposition.

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Table 3: Relative product distributions obtained in electrocracking gas reaction as a function of Ni loading of the catalyst

Ni(Wt %)	2.5	5	7.5	10	12.5	15
CH ₄	0.3	0.9	1.0	2.2	3.8	3.7
C ₂ H ₄	27.8	28.4	29.8	31.1	33.6	33.9
C ₂ H ₆	21.0	19.6	18.5	17.4	16.3	16.0
Unreacted C ₂ H ₂	3.4	3.9	3.8	4.2	4.3	4.5
C ₃	4.5	5.2	5.4	5.9	6.2	6.4
C ₄₊	13.6	13.3	14.1	14.2	11.7	10.5
C ₅₊	18.0	17.2	15.7	15.4	13.2	13.8
Liquid Hydrocarbons	11.4	11.5	11.7	9.6	10.9	11.2

Reaction conditions as in figure 3.

Table 4: Catalyst lifetimes in electrocracking gas reaction as a function nickel atom loading of the catalyst. Lifetime is defined with respect to the first appearance of unreactant C₂H₂ in the effluent stream

%Ni	2.5	5	7.5	10	12.5	15
Time on stream(h)	6	5	4	3	3	3

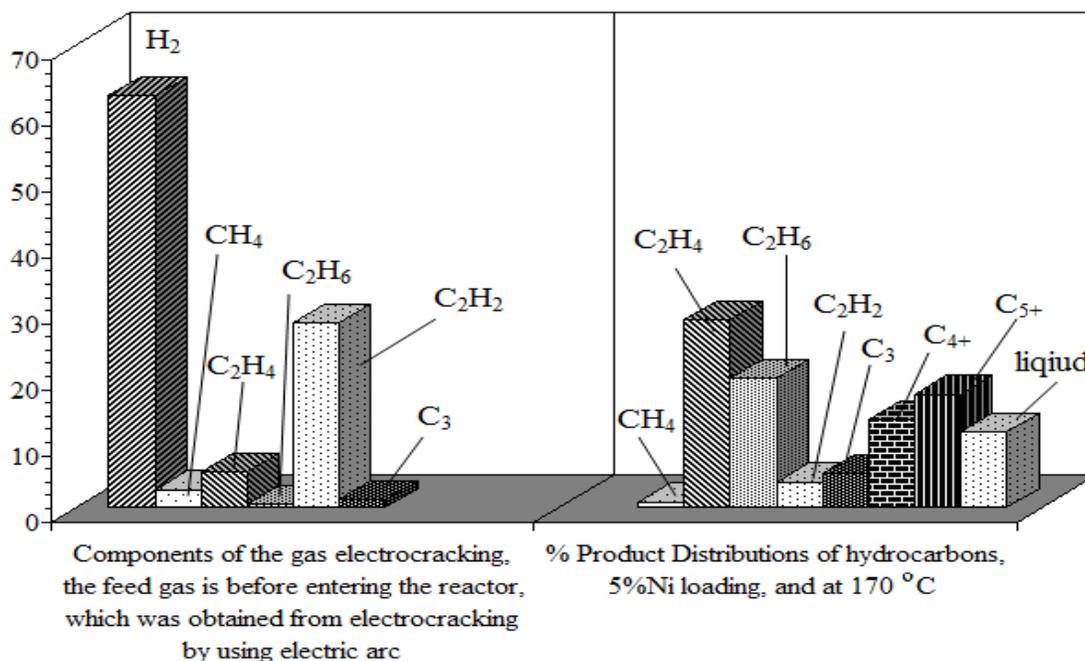


Figure 4: Components of the raw electrocracking gas and the product distribution at a temperature 170 °C and 5% Ni catalyst

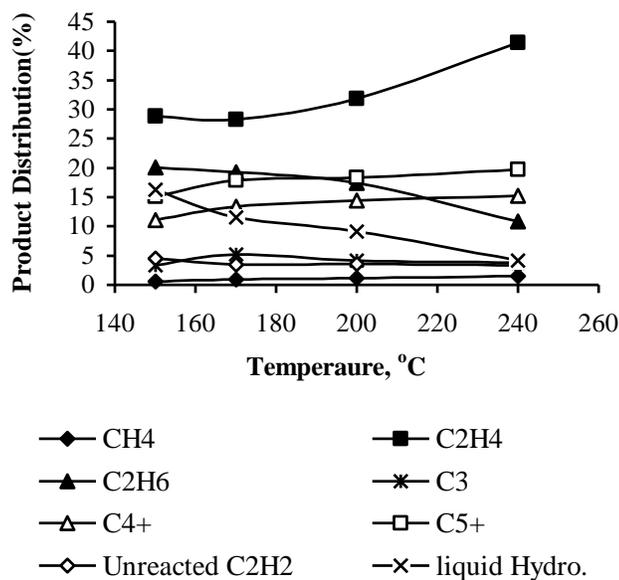


Figure 5. Product distribution as function of conversion temperature in gas electrocracking reactions

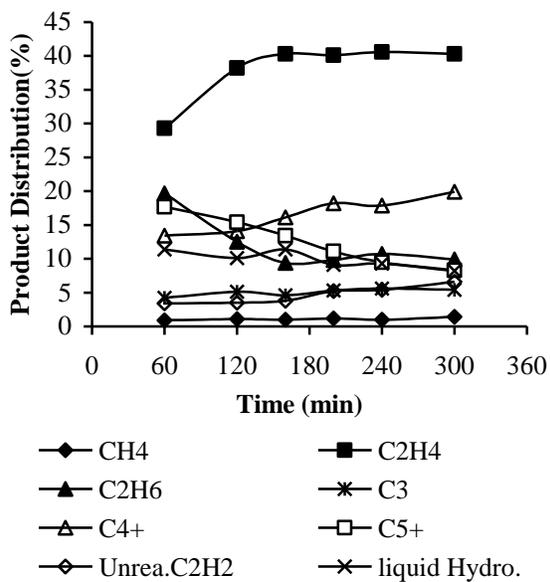


Figure 6: Product distribution as function of conversion time in gas electrocracking reactions

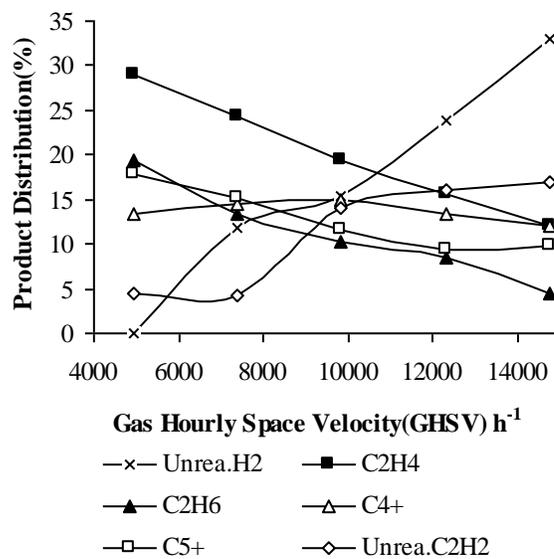


Figure 7: Product distribution as function of gas hourly space velocity (GHSV) for feedstock of gas electrocracking reactions

Table 5: Effect of variations of conversion temperature on the relative product distributions obtained during reactions of electrocracking gas

Temperature(°C)	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃	C ₄₊	C ₅₊	Unr.C ₂ H ₂	Liquid	%conv.
150	0.6	28.9	20.1	3.4	11.1	15.1	4.5	16.3	100
170	0.9	28.3	19.3	5.2	13.4	17.9	3.5	11.5	100
200	1.2	31.8	17.4	4.1	14.4	18.4	3.6	9.1	100
240	1.5	41.4	10.8	3.8	15.2	19.7	3.4	4.2	100

Reaction conditions as in figure 5

البلمرة المحددة للاستيلين الناتج من غاز التكسير الكهربائي وبوجود الهيدروجين على العامل المساعد Ni/ CNFs

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الخلاصة

تم إجراء البلمرة المحددة للاستيلين لنظام تدفق مستمر من غاز التكسير الكهربائي وبوجود الهيدروجين باستخدام عامل مساعد محضر بطريقة الإشباع على شكل عالق من النيكل المحمول على الكربون اللينفي الدقيق. نماذج العامل المساعد تحتوي على (5.0 Wt.% Ni) وهي قادرة على هدرجة الاستيلين بشكل كامل عند زمن 5 ساعات وبدرجة حرارة 170 °C، حيث يشكل الاستيلين 27-29 % والهيدروجين 61-64 % من النسبة المئوية لمكونات غاز التكسير الكهربائي الناتج من مخلفات زيت الديزل. لقد كانت كمية الايثان والاثيلين تكافؤ تقريباً نصف نسبة الاستيلين المتحول مع نسبة من البروبان، كذلك تكون الميثان والبروبيلين بكميات واطنة. بالإضافة لذلك تتحول النسب الباقية من الاستيلين الى هيدروكربونات ثقيلة من خلال البلمرة المحددة. توزيع النواتج السائده هي الالكينات الخطيه (C₄₊- C₅₊) يتبعها الالكينات المتفرعة (الايروبوتين والايروبينتان)، وكميه ضئيله من الداينات. النواتج الاخرى تظهر على شكل هيدروكربونات سائله (الزيت الاخضر). التجارب المختبرية تم اجراءها على مفاعل ذو سرير ثابت، وعند الضغط الجوي الاعتيادي، وباستخدام السرعة الحجميه لغاز التغذية بالساعة (غاز التكسير الكهربائي الحاوي على الاستيلين) بزمن 5920 h⁻¹ والمساوي الى سرعة جريان (30 ml/min) من غاز التغذية.