

- Bachelor Thesis -

Preparation and comparison of different types of carbon based heterogeneous catalysts and their application in selected reactions

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Abstract

This research projects general aim was to develop environmentally friendly heterogeneous catalysts based on carbon, to study their specific characteristics determine their suitability for reactions of interest.

For this purpose three different preparation methods were chosen and the resulting catalysts tested in esterification reactions.

Activated carbons prepared by three different methods were studied in esterification reactions for the production of flavors.

The carbon material is known for having exceptional textural and chemical properties. It is not hazardous and therefore easy to dispose. From this point of view it is of special interest to investigate whether it is possible to increase the sustainability by valorizing biomass waste as a feedstock and hereby encourage the manufacturing of added value products.

After their preparation the activated carbons were characterized by physical (nitrogen adsorption-desorption at 77 K) and chemical (point of zero charge, elemental analysis) analysis, before their application in the reactions mentioned before.

Evaluation of the data received from the analysis and the esterification reactions shows that the corn cob based biomass carbon combines excellent textural and catalytic properties and is therefore a suitable alternative for conventional catalysts.

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1) Introduction

The twentieth century was the era of chemistry finding its way into the everyday life of the modern society. Few aspects of today's daily routine are not related products processed by the chemical industry.

On the downside, however, the chemical industry is responsible for a variety of pollutions harmful to the human health and the environment. Though this was never the intention, when the processes were developed, the negative effects showed more and more as time passed. [1, 5]

In spite of Thomas Jefferson's criticism concerning these environmental concerns in 1789, the attitude towards them only changed during the last decades. In 1987 the Committee on Environment and Development of the United Nations (Brundtland Commission) drew attention to the issue and stated that a sustainable development is "*[...] meeting the needs of the present without compromising the ability of future generations [...]*". From that time on a general debate on how to achieve a more ecological development in the future was launched. [5]

The term 'Green Chemistry', which stands for a concept aiming for the encouragement of groundbreaking chemical technologies to potentially diminish the creation or utilization of hazardous feedstocks, additives or (by-) products, was shaped in the early 90s by the Environmental Protection Agency (E.P.A.). Soon after that the twelve principles of green chemistry were published by Paul Anastas and John Warner. Nowadays they are widely accepted as a methodology to realize sustainability. [1]

The twelve principals of green chemistry demand inter alia the application of catalysts whenever possible (point 9) as well as the substitution of conservative raw materials by renewable feedstocks (point 7). [1]

These points are going to be addressed hereafter because the target of this work is to determine the comparison of carbon based heterogeneous catalysts that were produced by different methods, one of them based on the organic waste material of corn cobs, as well as the determination whether they are suitable replacements for conventional catalysts and if so, which is the best.

If the activated carbons turn out to have good catalytic properties, they may be a decent alternative for the chemical industry since they also have the advantages of not being

hazardous (addresses point 3 of the principles of green chemistry), very easy disposal and, in the case of the biomass based catalyst, cheap production using an environmentally friendly feedstock. [1]

2) Theoretical Basics

2.1) Catalysis

2.1.1) Definition

A catalyst is “a compound that increases the rate of a chemical reaction, but which is not consumed by the reaction” [9] as stated by Wilhelm Ostwald around 1900. It lowers a specific reaction’s activation energy without affecting the reaction equilibrium or the Gibbs free enthalpy of either educts or products. The catalyst is regenerated, when the product is formed, although it may have changed in structure and composition. [5, 9]

2.1.2) Types of Catalysis

Catalysis in general can be subdivided into homogeneous and heterogeneous catalysis. This division is based on the phase reactants and catalysts are in. [2, 5]

For homogeneous catalysis both catalyst and reactants are in the same phase. Consequently it is either a liquid-liquid or gaseous-gaseous system. In homogeneous catalysis every unit can serve as an active site leading to excellent activity and selectivity. On the downside it is rather difficult and energy intensive to separate a homogeneous system. It is necessary to distillate the reaction products or, in case of thermally instable components, use a precipitation method. [2, 5]

In contrast reactants and catalysts are in different phases for heterogeneous catalysis, as the name suggests. The catalyst is mostly solid and the reactants either liquid or gaseous. Activity is generally lower in heterogeneous catalysis, since only active sites on the surface are accessible. Additionally factors such as external/internal diffusion and adsorption/desorption, which are related to the catalysts’ physical shape, have to be taken into account. Yet their thermal stability, simple recovery and reusability (after reactivation) make heterogeneous catalysis an attractive alternative for homogeneous catalysis. [2, 5]

2.2) Activated Carbon

2.2.1) Definition

Activated Carbon (AC) is a highly porous matter that is (mainly) formed by carbon atoms that are arranged in a specific structure. This structure consists of ring configurations which are arranged in layers and so shape a disordered three dimensional network. There are a few physical properties used to characterize its qualities. Among these properties are the AC's pore volume, pore size distribution and total surface area. Its chemical surface composition is another important factor that influences the carbons characteristics. [7, 11]

2.2.2) Raw Materials and Processing

Activated Carbon is normally prepared by carbonization of organic matter. Possible feedstocks are theoretically almost all organic materials, including coal, peat, wood, some organic waste materials or synthetic organic polymers. Limiting factors are mostly economic reasons and the wish for consistent AC quality with certain traits.

2.2.3) Carbonization and Activation

The production of AC requires three steps, which are independent from the raw material used. These steps are:

1. Preparation of the raw material
2. Carbonization
3. Activation [11]

The order of carbonization and activation might change, depending on the type of activation chosen.

The exact preparation of the raw material differs greatly, depending on the material and will therefore not be discussed at this point. After preparation of the material the carbonization is carried out. This is in fact nothing else than a pyrolysis of the organic material at around 800 – 1000 °C under inert atmosphere. This way the matter's carbon proportion is raised and the number of heteroatoms is decreased. [7]

To develop porous structure and improve textural properties in the carbonized material it needs to be either physically or chemically activated. [7]

Physical (also called thermal) activation, is a process of selective gasification due to different reactivity of the carbon atoms. They are removed by reaction with carbon dioxide or water vapor at around 800 – 900 °C and therefore leave a more porous carbon. [7]

In opposition to the physical activation the chemical activation takes place before carbonization. To achieve higher porosity the raw material is treated with chemicals such as zinc chloride, phosphoric acid or potassium hydroxide which then engage in a reaction with the heteroatoms. This way carbonization yields are enhanced since there is no removal of carbon atoms. [7]

During the process of activation macropores (> 50 nm) are shaped first, followed by mesopores (2.0 – 50 nm) that are created in the macropores' walls. Micropores (< 2.0 nm) are formed last. **Figure 1** gives an impression of the matrix of an average AC. The matrix can be altered by varying feedstock, method of carbonization and activation. Characteristic features of the AC's properties are significantly influenced by its matrix.

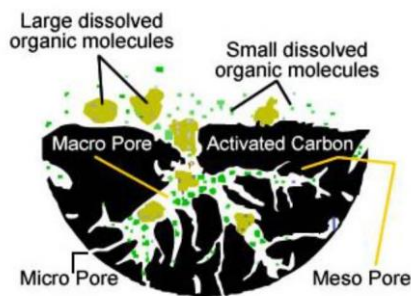


Figure 1: Schematic representation of an activated carbon porous matrix [11]

2.3) Adsorption

2.3.1) Definition

There are three terms that are necessary to describe the process of adsorption: the adsorptive, the adsorbent and the adsorbate. The former describes particles (atom, molecules or ions) from a fluid phase that are added to the surface of a solid (liquid) phase, the adsorbent. In the course of this process there is a change of concentration at the phase boundary due to the accumulation of the adsorptive on the adsorbent's surface. The adsorbed particles are referred to as adsorbate. High pressures and low temperatures support the adsorption, since it is an exothermic process.

This process is often reversible by reversing the conditions and then called desorption. [4] [9] [11]

2.3.2) Adsorption Isotherm

The adsorption isotherm is the graph that states the correlation between the amount of particles adsorbed and the pressure respectively concentration at a constant temperature. The former applies for gases, the latter for solutions. This means that at a constant temperature there is a dynamic equilibrium between the adsorptive and the adsorbate established, which shifts with increasing pressure. [4] [11]

Various models have been developed to describe this correlation, such as the Langmuir, the Freundlich or the Brunauer, Emmet and Teller (BET) model. [11]

For this thesis the BET method is used. It is based on the adsorption of nitrogen at 77 K, which is the corresponding gas condensation temperature. With this method a porous solid's surface area can be estimated and the adsorption isotherm obtained gives further information about the adsorbent's properties. [9]

The first step is to transform the physisorption isotherm into the 'BET plot' and use it to calculate the BET monolayer capacity by the BET equation:

$$\frac{p/p^\circ}{n(1 - p/p^\circ)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} (p/p^\circ) \quad (1)$$

p/p° ... relative pressure

n ... specific amount of gas adsorbed [mol]

n_m ... monolayer capacity [mol/g]

C ... exponentially to the energy of monolayer adsorption related parameter [14]

To calculate the specific surface area of the adsorbent [m^2/g] by the following equation one must know the monolayer volume [$\text{cm}^3 \text{g}^{-1}$]. [9]

$$S_{BET} = n_m \cdot A_m \cdot N_A \quad (2)$$

s ... specific surface area [m^2/kg or m^2/g]

n_m ... monolayer capacity [mol/g]

A_m ... area occupied by one molecule [$\text{m}^2/\text{molecule}$]

N_A ... Avogadro number [$6.023 \times 10^{23}/(\text{molecules mol})$]

The adsorption isotherm often has an adsorption and a desorption branch. This is caused by different properties of condensation and evaporation from the pores, which are influenced by the mesoporous void volume and the pore size distribution. Hence they can be determined by analyzing this part of the isotherm, which is called hysteresis. [9]

2.3.2.1) Types of adsorption isotherms

The International Union of Pure and Applied Chemistry (IUPAC) defined six types of adsorption isotherms to categorize the tremendous number of possibly obtainable isotherms of different gas-solid adsorption systems. [11]

The graphs in **Figure 2** below display the different types plotting the amount of nitrogen adsorbed over the relative pressure.

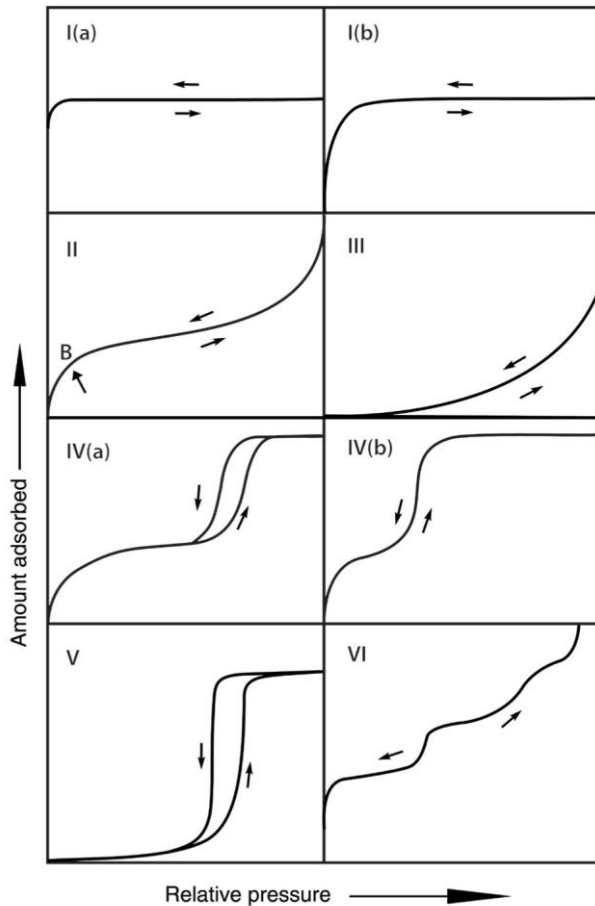


Figure 2: Classification of physisorption isotherms. [14]

The different types of adsorption isotherms are typical for certain surface properties of porous particles but they can only be applied for the adsorption of single component gas at condensation temperature. [11]

Type I: The course of the graph is typical for monolayer adsorption on an ideal surface with micropores. The surface is saturated and there are no interactions between the adsorbed particles. The accessible micropore volume limits the uptake. Interactions between adsorbent and adsorptive cause a steep uptake at low relative pressures. [9, 11, 14]

(a) Isotherm typical for materials possessing primarily narrow micropores (< ~ 1 nm) [14]

(b) Isotherm typical for a broader pore size distribution up to the size of narrow mesopores (< ~ 2.5 nm) [14]

Type II: For this type there are multilayers beginning to form at point B. The shape is typical for either non-porous or macroporous adsorbents. There is no hysteresis and therefore no mesopores as well. [9, 11]

Type III: A rarely observed type of adsorption isotherm which is characteristic for macroporous adsorbents. The graph suggests that the particles are bound stronger to the surface as it becomes more occupied, which means there are lateral interactions. Again there is no hysteresis. [9, 11]

Type IV: This type has a hysteresis loop, which is characteristic for a mesoporous adsorbent. As with *Type II* multilayers are forming at point B followed by capillary condensation. [9, 11, 14]

(a) The critical pore size of ~ 4 nm is exceeded and therefore a hysteresis behavior occurs. [14]

(b) Pore width remains below the critical value. Hence reversible isotherms are obtained. [14]

Type V: Just as the *Type IV* above this isotherm possess a hysteresis loop which is usually observed for a mesoporous materials. The shape suggest, like for *Type III*, lateral interactions. [9, 11]

Type VI: This shape of adsorption isotherm is typical for a uniform surface and layer-by-layer adsorption. [11]

The specific shape of the hysteresis loop is also characteristic for the pores properties. It gives information on the pores shape and distribution as displayed in **Figure 3** below.

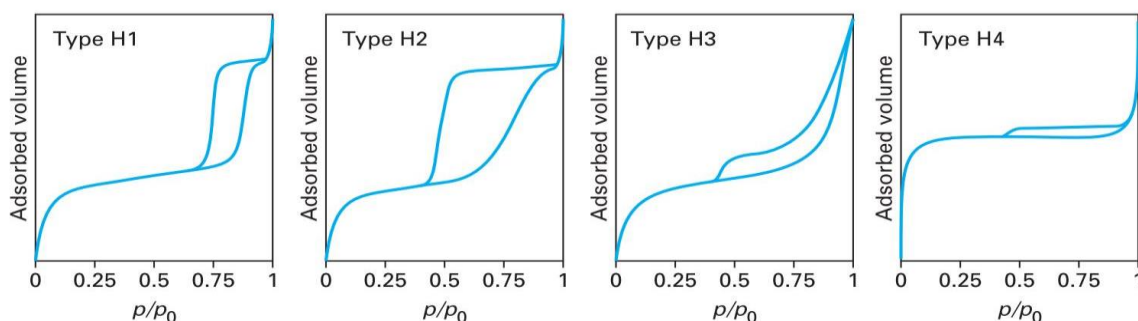


Figure 3: Hysteresis behavior for different types of pores: adsorbed amount as a function of relative pressure. [9]

The meaning of the four shapes of hysteresis are explained by the following **Table 1**.

Type	Shape	Uniformity	Distribution
H1	almost cylindrical	uniform	narrow
H2	almost cylindrical	non-uniform (more complex)	narrow
H3	slit shaped	uniform	-
H4	slit shaped	non-uniform	-

Table 1: Characteristic properties of different types of hysteresis [9]

2.4) Characterization

2.4.1) Physical Characterization

The AC's physical properties are determined by recording the adsorption isotherm for nitrogen adsorption-desorption at 77 K.

Based on this information the total surface area (S_{BET}) can be estimated by the BET-method. The total pore volume (V_p) results from the total quantity of nitrogen adsorbed at $p/p_0 = 0.99$. The mesoporous and microporous void volume (V_{meso} , V_{micro}) can be calculated by the Barret-Joyner-Halenda-method (BJH) respectively the t-method by Greeg and Sing.

2.4.2) Chemical Characterization

2.4.2.1) Point of Zero Charge

The AC's surface composition, especially the presence of functional groups containing oxygen, greatly influences the catalysts properties. Since the surface charge of the particle depends on the pH value in an aqueous solution due to dissociation of acidic (respectively basic) groups. This behavior results in a negatively (positively) charged particle surface under neutral conditions. If the pH value is decreased (increased) the surface groups dissociation equilibrium is shifted until the net electrical charge of the catalyst particle eventually equals zero. This pH value is called the point of zero charge (pzc) or isoelectric point (IEP). [9, 13]

Consequently the particles surface charge and therefore its adsorption properties can be influenced by choosing a certain pH value for the solution. A value greater than the pH_{pzc} leads to a negatively charged surface and therefore causes the adsorption of

cations while pH values smaller than the pH_{pzc} favor the adsorption of anions. This effect is illustrated by **Figure 4** for a mineral, that possesses very similar features as an AC. [9][13]

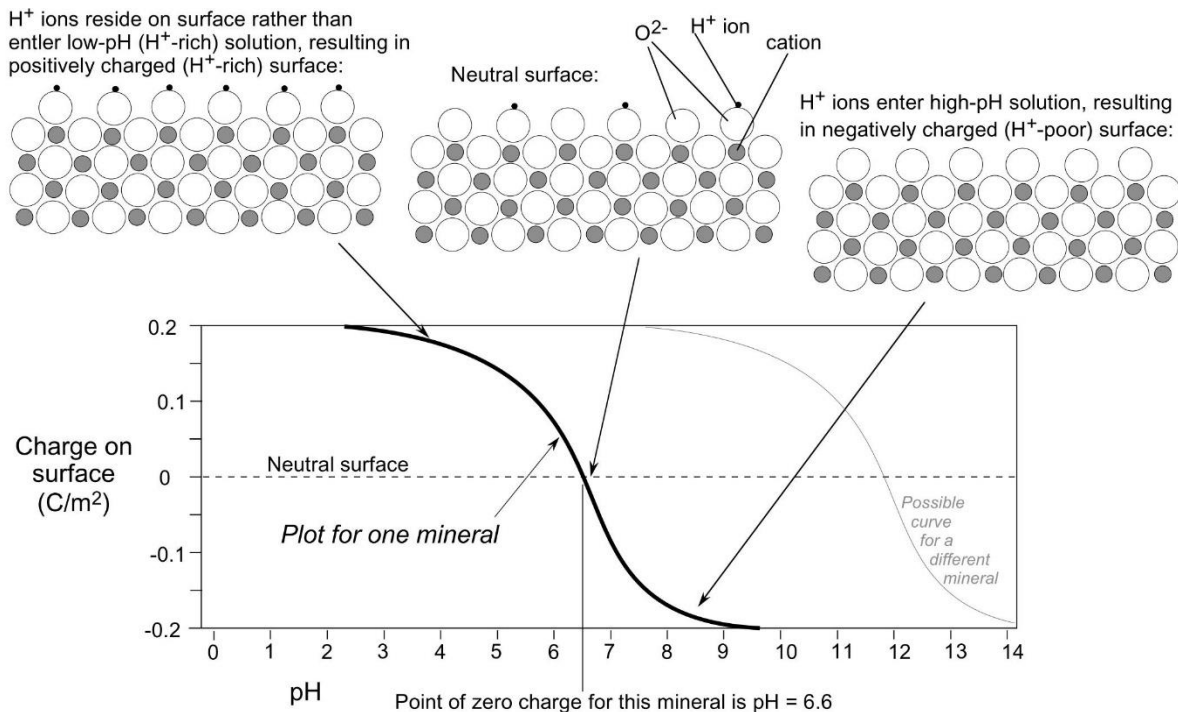


Figure 4: Plot of the surface charge for a mineral [13]

The point of zero charge is often determined by a classic acid/base titration. An alternative is the so called mass titration method. In contrast to a titration method there is not a constant amount of catalyst and increasing amounts of acid/base added but an increasing quantity of carbon is added to a certain amount of distilled water. The suspensions pH value will adjust according to the amount of carbon added. At some point, when there is an excess amount of AC added to the water, the pH value reaches a steady limit, the pH_{pzc} . [10]

2.4.2.2) CHNS Elemental Analysis

Elemental Analysis is used to gain information about the AC sample's chemical composition. The elements carbon, hydrogen, nitrogen and sulfur can be determined by oxidization and subsequent reduction of nitrogen oxides to nitrogen gas. The gases can then be qualitatively and quantitatively detected by e.g. gas chromatography followed by thermal conductivity detection or a series of thermal and infrared detectors. [12]

2.5) Test Reactions

To compare the different AC's properties in practice, esterification reactions using acetic acid and three different types of alcohol are carried out as test reactions. The reaction of acetic acid with octanol, hexanol and isoamyl alcohol should result in receiving the flavors orange, banana and pear.

Esterifications are conventionally either catalyzed by heterogeneous solid acids or by homogeneous mineral acids, such as sulfuric acid or hydrochloric acid. The general reaction mechanism is displayed in **Figure 5**.

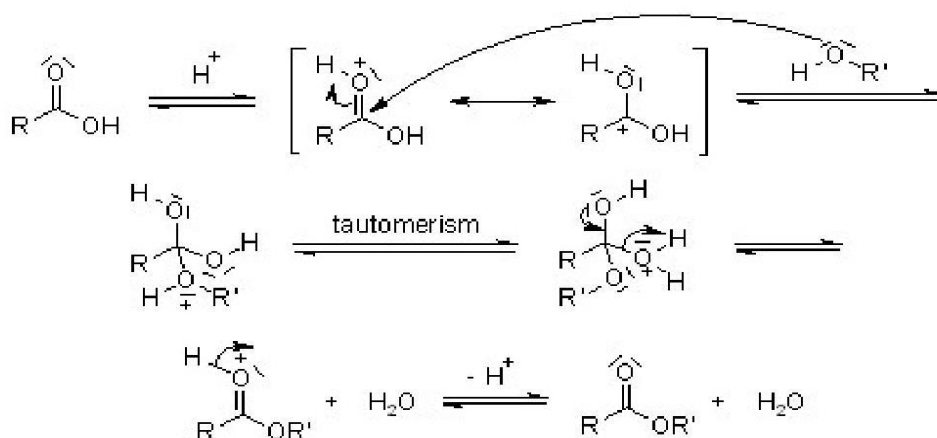


Figure 5: Acid catalyzed esterification mechanism [3]

Esters are produced in large amounts since the demand for artificial flavors is high. Therefore the chemical industry could benefit greatly, if conventional catalysts could be replaced by cheap and environmentally friendly carbon based catalysts because of their nonpolluting properties in production and disposal and the advantages of heterogeneous catalysis over homogeneous catalysis. [6]

3) Experimental Part

3.1) Types of Carbon

3.1.1) Synthetic Carbon

The synthetic carbon is based on a polymer synthesized by the sol gel method. The first step for this method was to prepare two aqueous solutions in sealable flasks of 5.6 g resorcinol, 0.106 g sodium carbonate, which acts as a catalyst in this reaction, and 114.4 ml of distilled water each. To dissolve the sodium carbonate the solutions were magnetically stirred before adding 7.6 ml formaldehyde. The exact amounts of chemicals used are displayed in the **Table 2** below. Afterwards the pH was adjusted to a value of 6.4 using six molar nitric acid, the flasks were sealed and the solutions magnetically stirred for one hour.

Solution	1	2	3	4
Resorcinol [g]	5.600	5.608	5.603	5.603
Sodium carbonate [g]	0.106	0.106	0.105	0.105
Water [ml]	114.5	114.5	114.5	114.5
Formaldehyde [ml]	7.6	7.6	7.6	7.6
Adjusted pH value	6.41	6.44	6.24	6.46

Table 2: Amounts of chemicals used and adjusted pH values for the sol gel synthetic carbon solutions [15]

The next step was a thermal treatment at 85 ± 3 °C for 7 days without stirring. Once the gel received during this process was cooled down to room temperature the content of both flasks was crushed, mixed and covered with acetone for 24 h to remove water from the pores. The gel was then filtered and the process of washing with acetone was repeated two more times before drying it at 85 ± 3 °C for three days, and then raising the temperature to 100 ± 3 °C for another 48 h. The gel's volume shrunk significantly during this procedure. [8]

To carbonize the polymer a pyrolysis was carried out in a silica reactor under nitrogen atmosphere ($\dot{V} = 150$ ml/min) using a high temperature furnace. The temperature ramp chosen is displayed in **Figure 6** and the carbon received was named RFC1.

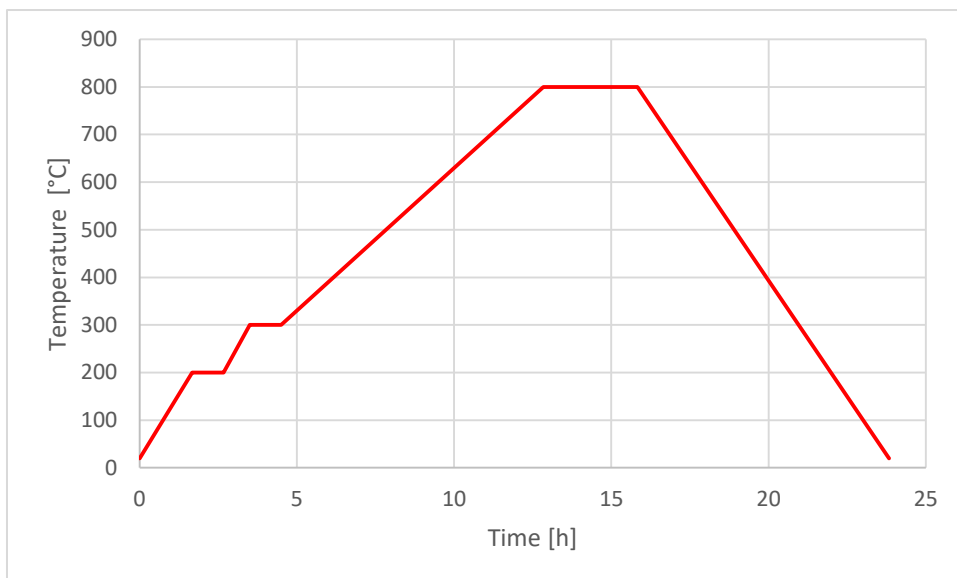


Figure 6: Temperature ramp for the RFC1 carbonization [15]

The same procedure (see Table X for the amounts of chemicals utilized) was then used to prepare another batch of carbon called RFC2. This batch of carbon was physically activated subsequently, as displayed in **Figure 7**, to receive the carbon RFC2CO₂. Heating and cool down took place under inert atmosphere (nitrogen, $\dot{V} = 150 \text{ ml}/\text{min}$), whereas the atmosphere was switched to CO₂ at constant 800 °C for the activation process.

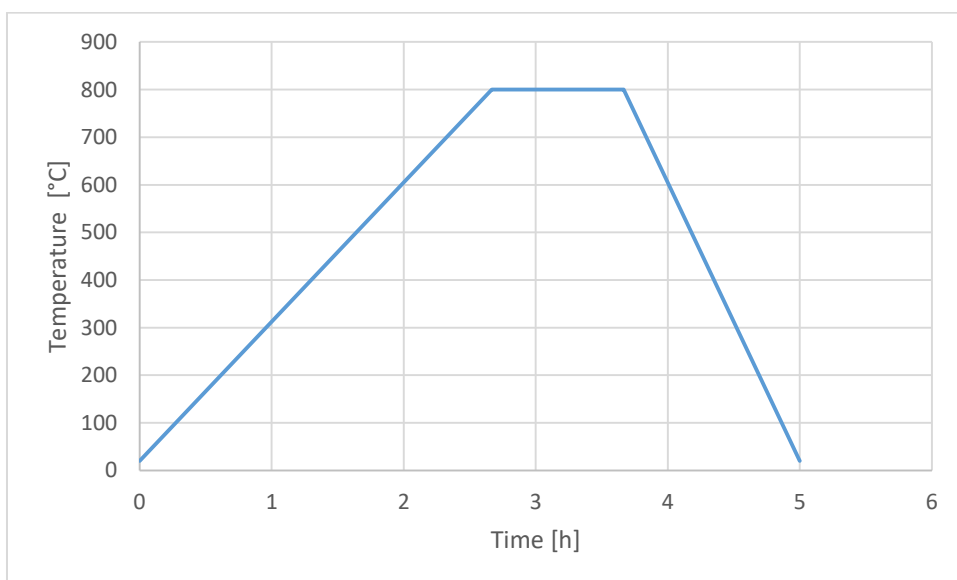


Figure 7: Temperature ramp for the RFC2CO₂ thermal activation [15]

3.1.2) Biomass Carbon

Per batch of biomass carbon 6 g of shredded corn cob were pyrolyzed and activated using the same type of silica reactor as for the production of the synthetic carbons. The temperature ramps used are shown by **Figure 8**. The pyrolysis takes place during the heating process under nitrogen atmosphere ($\dot{V} = 150 \text{ ml}/\text{min}$) and is then, at 800 °C, switched. Activation time and atmosphere were varied to achieve the best results possible in terms of total surface area and porosity.

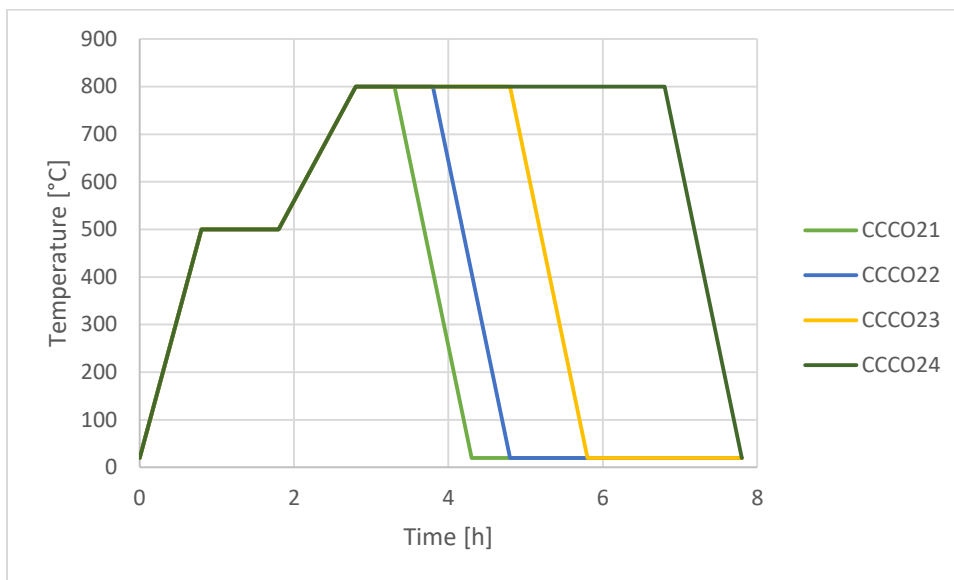


Figure 8: Temperature ramp for the biomass carbon carbonization and activation [15]

For the first activation attempt a mixed atmosphere of $150 \text{ ml}/\text{min}$ nitrogen and carbon dioxide each was chosen and the temperature was kept at 800 °C for half an hour. The next attempts were carried out under pure carbon dioxide atmosphere ($\dot{V} = 150 \text{ ml}/\text{min}$) and the activation time was doubled each time until a maximum at 4 h. For cool down the atmosphere was switched back to nitrogen.

The largest total surface area was received at 2 h activation time and therefore this procedure was repeated times two more and the product was mixed to increase the yield of CCCO_2 .

3.2) Treatment

The previously prepared carbons RFC1, RFC2CO₂ and CCCO₂, as well as the commercial activated carbon Norit GAC 1240 M-2035, which will be referred to NC in the following, were then chemically treated to add (acidic) functional groups to their surfaces and therefore alter their catalytic properties such as selectivity. The choice of methods relied on the research group's experience.

3.2.1) Nitric Acid Treatment

All carbons were subjected to a nitric acid treatment. For this purpose 17.9 ml nitric acid (13 M) per gram activated carbon concentrated were diluted with 2.1 ml/g distilled water. The AC was given into a glass balloon before adding the diluted nitric acid. The suspension was then heated under reflux to 90 °C in an oil bath and kept at this temperature for six hours, while being magnetically stirred. The procedure was followed by cooling to room temperature decanting of the carbon. The activated carbon was then alternating washed with distilled water and decanted until a pH value of about 5 was reached. At last the AC was dried at a temperature of 85 ± 3 °C for 48 h and the letter N was added to all the carbons names, so from now on they will be referred to as NCN, RFC1N, RFC2CO₂N and CCCO₂N.

3.2.2) Sulfuric Acid Treatment

The nitric acid treatment was followed by a sulfuric acid one, but due to the very time consuming preparation of RFC2CO₂ and CCCO₂ there were insufficient amounts to undergo another treatment. Thus only the carbons NCN and RFC1N (half of each) were treated with sulfuric acid.

The carbon and 20 ml concentrated sulfuric acid per gram carbon were added to a two-necked balloon with reflux. The suspension was magnetically stirred and heated under nitrogen atmosphere in an oil bath to 150 °C. It was kept at this temperature for seven hours.

The processes of cooldown, decanting, washing and drying were carried out in analogy to the nitric acid treatment.

3.3) Grinding and Classification

The treated and dried carbons were then ground using a blade mill and thereafter classified with a sieve column composed of a 180 μm (mesh size #80) and a 150 μm (mesh size #100) to receive a particle size of less than 150 μm and consequently avoid mass transfer effect in the following reactions.

3.4) Characterization

The methods described in chapter 2.4), viz. nitrogen adsorption/desorption, elemental analysis and the point of zero charge were employed to characterize the catalysts properties.

3.4.1) Physical Characterization

For the record of the nitrogen adsorption isotherm at 77 K was utilized. The total surface area and the total pore volume were both determined by the BET equation, the former at $p/p_0 < 0.024$, the latter at $p/p_0 < 0.95$.

The mesoporous volume was calculated by the Barret-Joyner-Halenda (BJH) method considering the cumulative volume of pores between 1.7000 nm and 300.000 nm diameter.

The microporous volume was estimated by the t-plot-method.

3.4.2) Chemical Characterization

3.4.2.1) Point of Zero Charge

For the determination of the point of zero charge a suspension of 0.1 g of AC and 1.0 ml of deionized water was prepared and left on a shaker for 24 h under inert atmosphere for the equilibrium between the carbons functional groups and the water to establish. The pH value measured afterwards is the limiting pzc since 0.1 g of carbon is in relation to the amount of water an excess amount according to the research group's experience.

3.4.2.2) CHNS Elemental Analysis

The elemental analysis was carried out by a Thermofinnigan Flash EA 1112 Series.

3.5) Reactions

To test the ACs' catalytic properties several esterification reactions were carried out involving three different types of alcohol (octanol, hexanol and isoamyl alcohol) and an excess amount of acetic acid each. So three reactions were carried with the same and therefore a total of 18 reactions were carried out. [6]

The first step was to add 15 ml of pure acetic acid and 0.25 g of AC to a 100 ml two-necked balloon with reflux and heat the suspension to 90 °C in an oil bath while stirring it magnetically. When the temperature was reached 15.0 ml of octanol respectively 12.0 ml of hexanol or 10.4 ml isoamyl alcohol (each corresponding to an amount of 0.09 mol) were inserted into the balloon. Samples were withdrawn during a time span of 30 h. For the first hour they were taken every 15 min, then hourly up to 8 h reaction time. The next sample was collected at 24 h and after that again hourly until 30 h reaction time. The samples were centrifuged, sealed and stored at a low temperature (-18 °C) until they were analyzed.

3.5.3) Sample analysis

Sample analysis was carried out by a Konic HRGC 5000B gas chromatograph using temperature ramps that fit the need of the different reaction products. The reaction products of all the esterification reactions were preheated to 50 °C. Afterwards the samples with octanol were heated to 100 C at a rate of 10 °C/min, whereas the samples of the reactions employing hexanol and isoamyl alcohol were then heated to only 70 °C at a rate of 5 °C/min.

4) Results

4.1) Yields of Carbon Preparation and Treatment

During the course of the carbon preparation and treatment the yields of activated carbon received in relation to the mass of educts used were recorded and are presented in the following.

The yield of each production step was calculated by dividing the received mass (output mass) by the input mass of educts. Afterwards the overall yield was calculated by multiplying the yields of all the previous steps.

The received yields for the commercial carbons NCN and NCNS are the highest but they are not informative because they only consider the nitric and sulfuric acid treatment. The yield of carbonization and activation for the Norit carbon are unknown. Therefore these yields are not comparable to the others.

The carbons RFC1 and RFC2 were prepared in the same way. Both were synthesized as explained in chapter 3.1.1 but despite being carbonized under the same conditions afterwards is the yield of RFC1 almost twice as big as the yield of RFC2 (see Table X on p. X in the attachment). This could be due to a possible leak in the carbonization assembly. If the atmosphere was not completely inert and oxygen got into the reactor, part of the carbon might have been oxidized.

In contrast to the RFC1 carbon the RFC2 was physically activated with CO₂ after carbonization to increase its surface area and pore volume. Due to partial gasification of the carbon atoms a mass loss of about 35 % was recorded (see **Fehler! Verweisquelle konnte nicht gefunden werden.**, chapter 12.2).

Unlike the RFC2 carbon the corn cob biomass was carbonized and activated in one step. Four batches were carbonized with increasing activation time (see chapter 3.1.2). As the activation time increased the yield of AC received decreased from about 25 % to 0 % yield for the reason that more carbon is gasified. At four hours activation time no carbon is left in the reactor. The average yield of the AC with the best properties (CCCO₂₂, CCCO₂₅, CCCO₂₆) was 18.54 %, which is about the same as for the RFC2CO₂ after carbonization and activation.

The yields for the nitric and sulfuric acid treatment were generally higher than 90 %, except for the sulfuric acid treatment of the RFC1N and the nitric acid treatment of

RFCCO₂. The losses here were higher due to floatation of the carbons in the acid and therefore higher losses during decantation.

The overall yields are displayed in **Table 3**. As mentioned at the beginning the yields of the first two ACs cannot be compared to the others but it is easily noticeable, that the yields of those carbons, that were not physically activated, are roughly three times as high as those of the physically activated carbons. Whether it is worth to accept these lower yields for the sake of better catalytic properties or not will be discussed in the following.

Carbons	Yield [%]
NCN	99.95
NCNS	99.79
RFC1N	51.36
RFC1NS	41.86
RFC2CO ₂ N	14.37
CCCO ₂ N	16.90

Table 3: Yields of activated carbon received after the total preparation process

4.2) Point of Zero Charge

After treating the ACs with nitric (and sulfuric) acid as described in chapter 3.2.1 and chapter 3.2.2 and washing the washing water's pH value became steady at a magnitude of about 4.5 – 5 as shown in **Table 4**. The washing water's pH value of carbons treated with sulfuric acid were in direct comparison to the same samples treated only with nitric acid slightly lower.

Carbons	pH (after washing)	pH(pzc)
NCN	4.9	3.98
NCNS	4.71	2.99
RFC1N	4.89	3.27
RFC1NS	4.6	2.88
RFC2CO ₂ N	4.64	3.21
CCCO ₂ N	4.73	3.58

Table 4: Points of zero charge measured for the different ACs

The same is the case for the point of zero charge values. They are all below seven, leading to the conclusion, that acidic functional groups, such as alcoholic or carboxylic acid groups, have been formed on the carbons' surfaces. During the nitric acid treatment those functional groups seem to have formed on the RFC carbons' surface ($pH_{pzc} \sim 3.2$), followed by the biomass carbon. The NCN showed the highest point of zero charge and therefore has the least amount of acidic functional groups. Also the acid strength of the sulfonic functional groups expected to be introduced by the sulfuric acid treatment, may explain the lower pH_{pzc} values obtained for these carbons.

The influence of the ACs' point of zero charge on their catalytic properties will be examined in chapter 4.6) later on.

4.3) Elemental Analysis

In addition to the estimation of the point of zero charge elemental analysis was carried out to gain further information about the ACs' chemical composition.

The analysis results for the commercial carbon match with the conclusions drawn from the pzc because the AC possessed only little hydrogen and nitrogen before the treatment but the proportion of hydrogen rose with each acidic treatment, the proportion of nitrogen in the AC increased after the nitric acid treatment and the concentration of sulfur went up in consequence of the sulfuric acid treatment (cf. **Table 5**). These changes indicate chemical changes in the AC surface chemistry and therefore the formation of functional groups.

Sample	C [%]	H [%]	N [%]	S [%]
NC	86,28	0,47	0,16	0
NCN	73,31	0,93	0,85	0
NCNS	67,39	1,67	0,5	0,18
RFC1N	62,9	1,12	0,77	0
RFC2	76,81	0	0	0
RFC2CO ₂	96,39	0	0	0
CCCO ₂	83,32	0	0,43	0

Table 5: Elemental analysis results for the ACs– Proportions of the elements carbon, hydrogen, nitrogen and sulfur contained

The carbons RFC1 and RFC2 were prepared in the same fashion (see chapter 3.1.1) hence it can be assumed that their chemical composition is virtually the same. If the results of the elemental analysis of the RFC2 carbon and the RFC1N are compared there is a significant increase in the concentration of hydrogen and nitrogen noticeable. Again this corresponds to the results of the estimation of the point of zero charge.

In accordance to the correlation of the determination of the point of zero charge and the results of the elemental analysis of the samples of commercial and synthetic carbon the same pattern can presumably be applied to the sulfuric acid treatment of the RFC1N and the nitric acid treatment of RFC2CO₂ and CCCO₂ and similar results for the elemental analysis can be expected.

4.4) Adsorption Isotherm

The nitrogen adsorption isotherms were recorded to determine the ACs' textural properties. Measuring points were chosen carefully and adjusted according to the experience gained in previous measurements with similar matter. This means the steps of relative pressure between the measuring points increase with increasing relative pressure since the graph is expected to start out very steep and level off towards the end.

The isotherms were measured after carbonization respectively physical activation and before nitric or sulfuric acid treatment. It was assumed that these treatments only alter the carbons' surface chemistry and although some effect over the porous structure may occur, it is expected to be of small extent.

4.4.1) Types of Adsorption Isotherms and Hysteresis

When analyzing the adsorption isotherms' shape it is noticeable that they differ very little (compare Figure 17 to Figure , chapter 12.1). They all resemble a Type I adsorption isotherm according to the IUPAC classification (chapter 2.3.2.1). This leads to the conclusion that the ACs are microporous solids, whose uptake is mostly limited by the accessible microporous volume.

The samples NCN, RFC1, RFC2 and RCF2CO₂ show more similarities to the adsorption isotherm Type I (b). This is typical for a broader pore size distribution, which

contains wider micropores and even mesopores. In contrast to that the Biomass AC (CCCO₂) has mainly narrow micropores since its graph resembles the adsorption isotherm Type I (a) almost perfectly.

The same pattern applies for the type of hysteresis. The isotherms of commercial and synthetic carbons display a hysteresis loop type H4, which indicates the presence of slit shaped non-uniform pores. This type often occurs in the case of micro-mesoporous carbon. [14]

Unlike the other samples the adsorption isotherm of the CCCO₂ sample has an almost unrecognizable hysteresis loop. If it was to categorize it would be comparable to an H4 hysteresis but it is so narrow, that there is next to no capillary condensation taking place.

4.4.2) Physical Properties

The activated carbons properties were calculated as explained in section 3.4.1) and listed in **Table 6** below. At first glance it becomes apparent that the commercial carbon possesses the largest total surface area (S_{BET}) as well the greatest total /micro- /mesopore volume ($V_{total} / V_{micro} / V_{meso}$), which might be due to the manufacturer's experience and equipment in terms of carbonization and activation. The order of samples following varies depending on the category looked at.

Textural properties	NC	RFC1	RFC2	RFC2CO ₂	CCCO ₂
S_{BET} [m ² /g]	1030	552	238	658	630
V_{total} [cm ³ /g]	0.557	0.280	0.094	0.295	0.251
V_{micro} [cm ³ /g]	0.304	0.155	0.083	0.175	0.214
V_{meso} [cm ³ /g]	0.171	0.096	0.007	0.060	0.0146

Table 6: The ACs' textural properties calculated from the adsorption isotherms

The RFC2CO₂ has the next largest total surface area, which is about 60 % the size of the NC's, followed closely by the CCCO₂ and the RFC1. The RFC2 possesses by far the smallest total surface area and the lowest pore volume (total, micro and mesopore), even though it was prepared in exactly the same manner as the RFC1. One explanation could be an oxygen leak during the process of pyrolysis, which would also explain the smaller yield (see chapter 4.1). For comparison of the other categories the RFC2 will not be mentioned anymore, since it has the lowest values anyway.

The total pore volume of the RFC1 is slightly lower than of the RFC2CO₂ and higher than of the biomass carbon but it possesses the lowest micropore volume and therefore the highest mesoporous volume in comparison of these three. The RFC2CO₂ has the largest total pore volume and in comparison to the RFC1 and CCCO₂ it ranks in the middle of both in terms of micro- and mesoporous volume. And even though the biomass carbon possesses the smallest total pore volume it has the largest microporous void volume and consequently the smallest mesoporous volume.

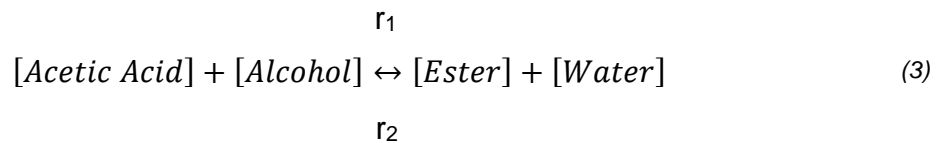
4.5) Conversion

The last step to determine the ACs' catalytic properties was to apply them as heterogeneous catalysts in esterification reactions. The conversion of acetic acid, alcohol and ester were determined by a GC analyzer in certain intervals.

To make the results better comparable a numeric kinetic model was applied.

4.5.1) Kinetic Model

The esterification reaction was initially regarded as an equilibrium:



The components were then referred to as:



Then the change in concentration was defined as:

$$\frac{dc}{dt} = k_1 \cdot c_A \cdot c_B - k_2 \cdot c_C \cdot c_D \quad (5)$$

And it was assumed that:

$$c_A = c_{A,0} - c_C \quad (6)$$

$$c_B = c_{B,0} - c_C \quad (7)$$

$$c_D = c_C \quad (8)$$

Therefore:

$$r_1 = k_1 \cdot c_A \cdot c_B = k_1(c_{A,0} - c_C)(c_{B,0} - c_C) \quad (9)$$

$$r_2 = k_2 \cdot c_C \cdot c_D = k_2 \cdot c_C^2 \quad (10)$$

In consequence the equations for the change of concentration for each component are:

$$\frac{dc_A}{dt} = \frac{dc_B}{dt} = -k_1 \cdot c_A \cdot c_B + k_2 \cdot c_C \cdot c_D \quad (11)$$

$$\frac{\Delta c_A}{\Delta t} = \frac{\Delta c_B}{\Delta t} = -k_1(c_{A,0} - c_C)(c_{B,0} - c_C) + k_2 \cdot c_C^2 = \alpha \quad (12)$$

$$\frac{dc_C}{dt} = \frac{dc_D}{dt} = k_1 \cdot c_A \cdot c_B - k_2 \cdot c_C \cdot c_D \quad (13)$$

$$\frac{\Delta c_C}{\Delta t} = k_1(c_{A,0} - c_C)(c_{B,0} - c_C) - k_2 \cdot c_C^2 = \beta \quad (14)$$

Hence the new component concentration after certain time intervals can be calculated by multiplying the concentration change with the time interval and addition of the old concentration value:

$$c_{A,new} = \alpha \cdot \Delta t + c_{A,old} \quad (15)$$

$$c_{B,new} = \alpha \cdot \Delta t + c_{B,old} \quad (16)$$

$$c_{C,new} = c_{D,new} = \beta \cdot \Delta t + c_{C,old} \quad (17)$$

For the initial calculations the values for k_1 and k_2 were estimated and Δt was set at 15 min. Afterwards k_1 and k_2 were numerically adjusted by the least squares method.

4.5.1.1) Model Accuracy

To verify the models accuracy parity graphs were drawn which display the numeric concentration values over the measured concentrations. The parity diagram showing the reaction utilizing NCN as a catalyst can be found below as an example. The other carbons' diagrams are in the appendix (chapter 12.1.1). It shows that the discrepancy is mostly less than 20 %, except for low concentrations of less than about 2 mol/l. However the absolute discrepancy of higher and lower concentrations is about the same. Overall the model possesses adequate accuracy to resemble the ACs' catalytic properties by reaction rate constants and concentrations.

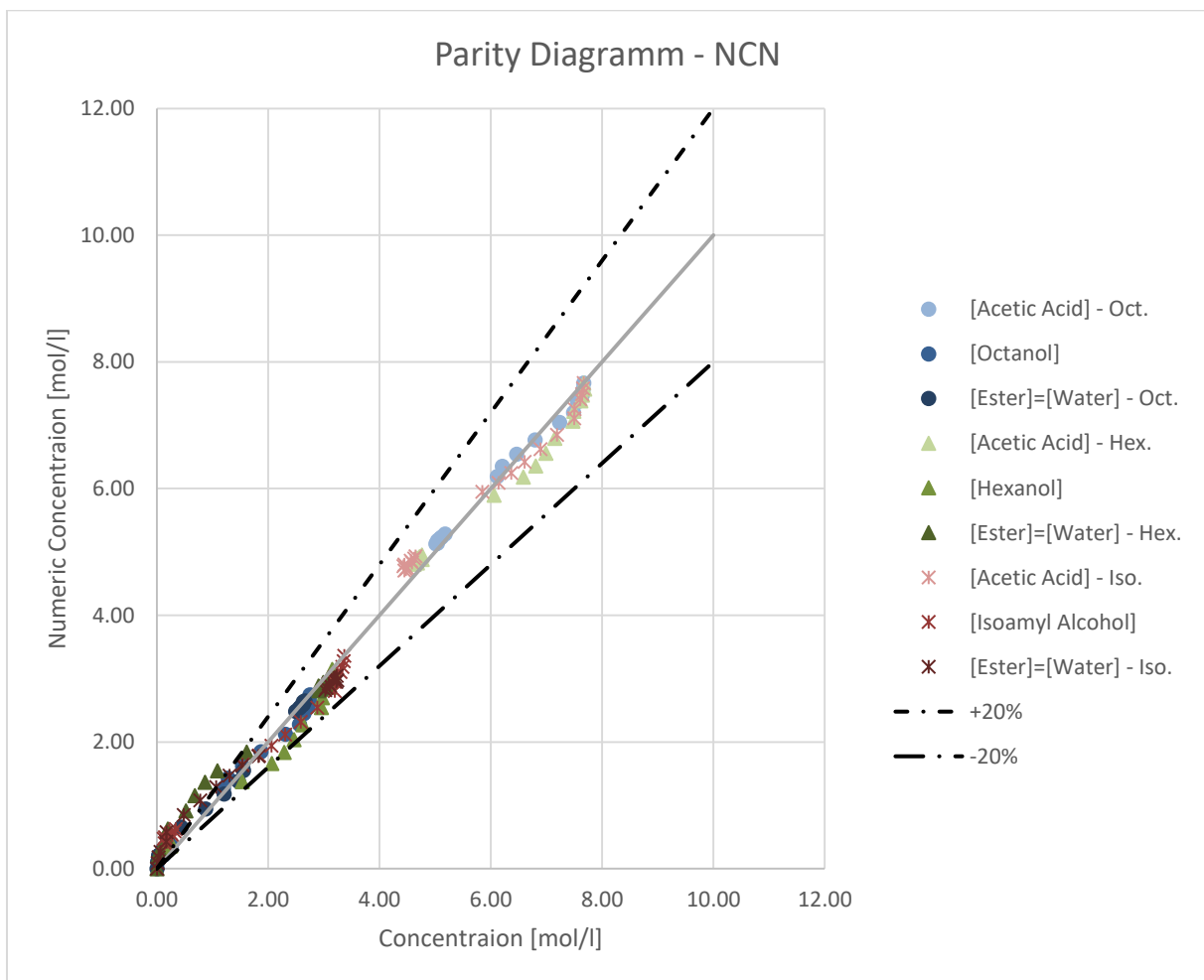


Figure 9: Parity diagram showing the relation of measured and numerically calculated concentrations for the reactions using NCN as catalyst

Additionally diagrams that show the concentration gradient of both measured and numerically calculated concentration values were made. The diagram (**Figure 10**) of the esterification reaction of acetic acid and octanol catalyzed by NCN gives an example of how congruent measured and calculated values are. The graphs also show

that there is an induction period at the beginning of the reaction. Initially the reaction rate increases slowly and then starts to accelerate. This might be explained by the sudden temperature drop after the initiation of the reaction. The acetic acid and the catalyst are added to the reactor first and then preheated to 90 °C before adding the alcohol, which has only room temperature, is added, as explained in chapter 3.5). This causes the reactants temperature to drop and consequently the reaction rate to slow down. It only starts to accelerate again as the reaction temperature of 90 °C is reached again.

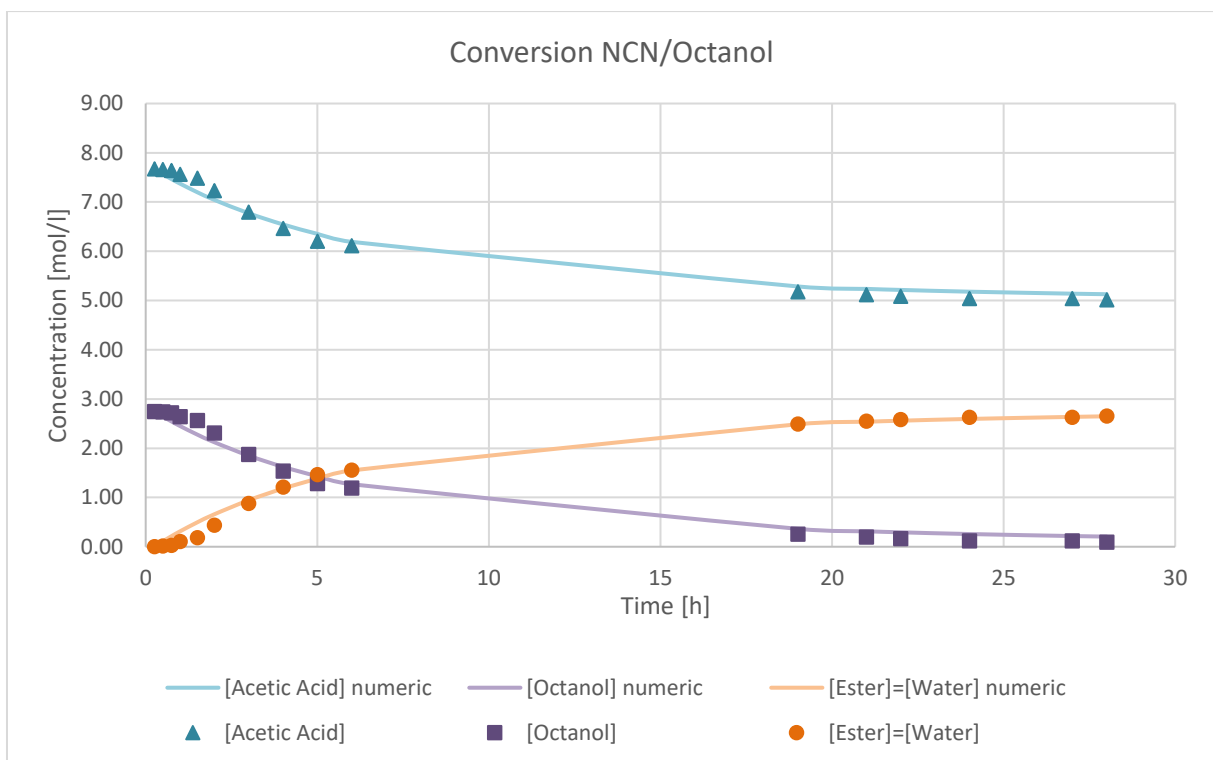


Figure 10: Comparison of measured and numerically calculated conversion of educts and products over time for the esterification reaction involving octanol and NCN as catalyst

4.5.2) Reaction Rate Constant

The constant k_2 was adjusted to equal zero, as displayed in **Table 7** below, since the conversion for every reaction strives against 100 %.

Carbon	Reaktion Rate Constant	Octanol	Hexanol	Isoamyl Alcohol
NCN	k1 [1/h]	0.0209	0.0170	0.0144
	k2 [1/h]	0	0	0
RFC1N	k1 [1/h]	0.0154	0.0112	0.0101
	k2 [1/h]	0	0	0
RFC1NS	k1 [1/h]	0.0175	0.0190	0.0089
	k2 [1/h]	0	0	0
RFC2CO ₂ N	k1 [1/h]	0.0167	0.0096	0.0090
	k2 [1/h]	0	0	0
CCCO ₂ N	k1 [1/h]	0.0216	-	0.0173
	k2 [1/h]	0	-	0

Table 7: Reaction rate constants calculated for each esterification reaction

Furthermore the reaction can be regarded as a reaction of the first order. The explanation is based on the following equation:

$$r = k' \cdot c_A \cdot c_B \quad (18)$$

But there is an excess amount of acetic acid. This means the concentration of acetic acid (c_A) can be regarded as constant. Therefore:

$$r = k \cdot c_B \quad (19)$$

With:

$$k = k' \cdot c_A \quad (20)$$

For the first reaction rate constant k_1 there are several tendencies visible. The first is that k_1 is for every AC the highest for octanol with only one exception. Secondly the chemical rate constant of the commercial and the biomass carbon are similarly high for the different alcohols, though there are no data for the esterification of hexanol with CCCO₂N used as a catalyst. Thirdly, the reaction rate constant of RFC1NS is the highest for this carbon and the highest for hexanol, which is the smallest non-branched alcohol molecule tested.

4.5.3) Comparison of Conversion at 8 h and 24 h

Two specific points of time were chosen to compare the conversion of ester in the different reactions, namely 8 h reaction time and 24 h reaction time. The point at 8 h time was chosen because it is in the steep part of the slope and differences between the reactions are strongly pronounced, whereas at 24 h, when the reactions are already close to 100 % conversion, differences in conversion between the different reactions are smaller.

Looking at the conversion values at 8 h (see **Figure 11**) it is noteworthy that the conversion of octanol is on average higher than the conversion of the other alcohols with the corresponding catalyst, except for the conversion of hexanol and the RFC1NS. However the highest conversions are achieved by the biomass catalyst at this point, closely followed by the commercial carbon catalyst. The synthetic carbon catalysts have the lowest conversion results with only one exception as mentioned before.

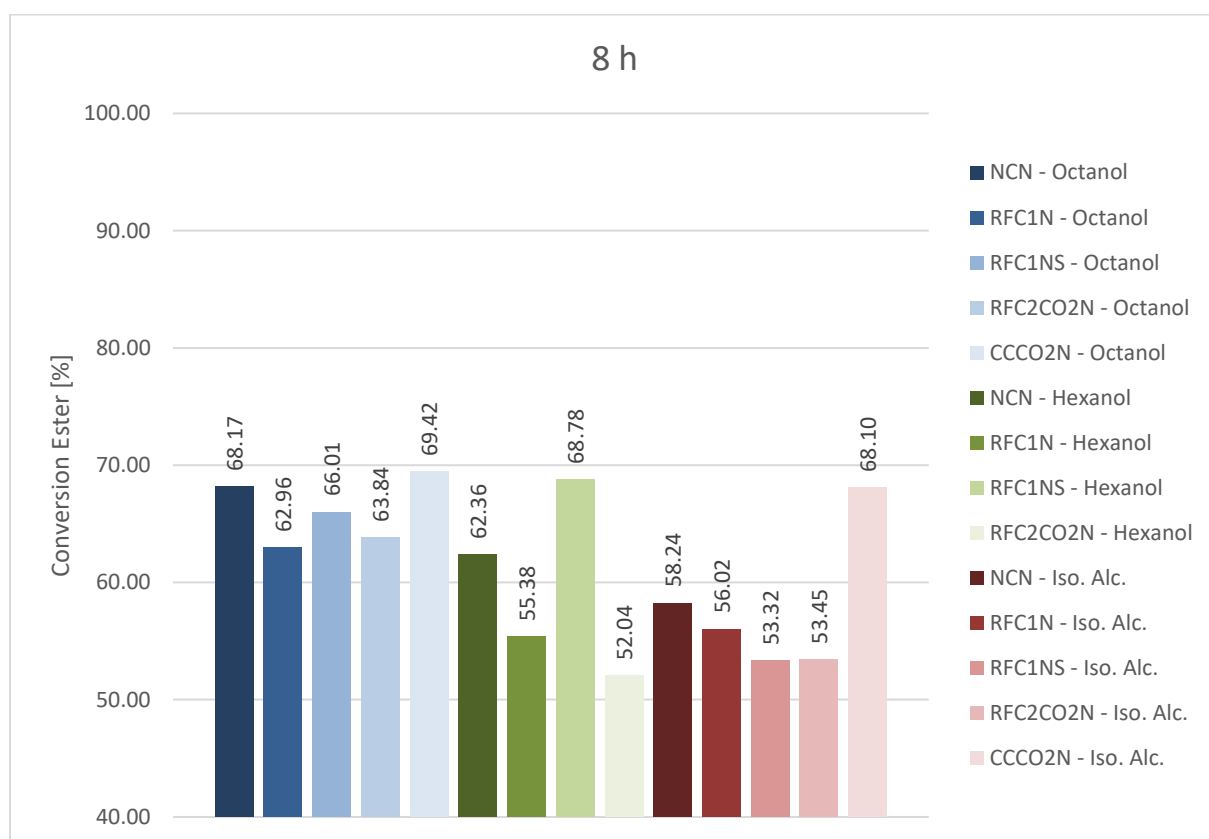


Figure 11: Conversion values to ester for each esterification reaction after 8 h reaction time

The conversion values at 24 h possess the same characteristics (see **Figure 12**). The only difference is in less variations between higher and lower conversion values since all the reactions will eventually reach about 100 % conversion. This difference is best

noticeable when the esterification of octanol with NCN as catalyst and hexanol with RFC2CO₂ as catalyst are compared. These two reactions show the greatest difference in conversion at 8 h as well as at 24 h but while the difference at 8 h is 17.38 % it is merely 4.46 % at 24 h. This is due to the fact that the catalyst does not influence the reaction equilibrium, it only shortens the time needed to reach it. Therefore a desired conversion may be reached faster with the right catalyst.

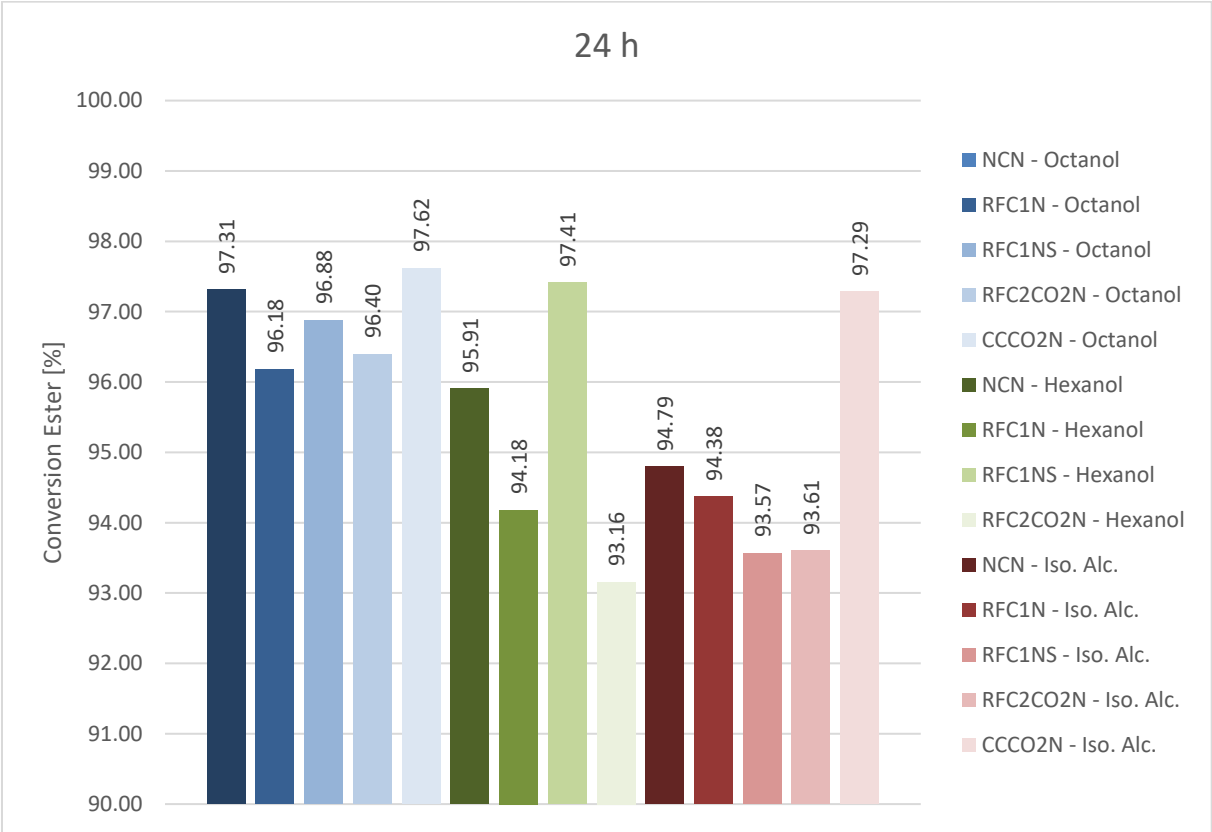


Figure 12: Conversion values to ester for each esterification reaction after 24 h reaction time

These results perfectly resemble the correlation of the reaction rate constant and the conversion rate. The characteristics of the ester conversion coincide with the high respectively low values for k_1 .

4.6) Correlation of Chemical and Physical Properties with Catalytic Results

To determine the ACs' relation of their textural and chemical characteristics and their catalytic qualities the most significant results, that is the total surface area, the total and microporous void volume, the reaction rate constant and the conversion at 8 h reaction time of each reaction, are listed in **Table 8**.

Looking at the values of the reaction rate constant's values and the corresponding conversion numbers it is important to note that they match completely as mentioned in the previous chapter. For the reactions with the highest reaction rate constants conversions are the highest and vice versa. With this in mind only the effect of the carbons properties conversion will be discussed in the following.

The results of the esterification reactions using octanol and isoamyl alcohol will be looked at first since they are similar and may lead to the same conclusions.

For both alcohols the conversions of the reactions catalyzed by NCN and the CCCO_2N are the highest. These carbons also possess the highest values for the pH_{pzc} and since the pH of the reactants is around two this higher point of zero charge causes the carbons' surface to be more positively charged than the synthetic carbons' surfaces and thus more attractive to the slightly acidic alcohols octanol and isoamyl alcohol.

The total surface area S_{BET} does not seem to have crucial impact on the ACs' catalytic properties since the conversion results of the biomass carbon are even better than the results of the commercial carbon, even though its total surface area is almost twice as large. The same applies to the total pore volume. Hence the other important factor, next to the point of zero charge, which greatly influences the catalytic properties is the microporous volume. The key element thereby is not only the absolute microporous volume itself but the relation of micro- and mesoporous volume, considering that the NCN's microporous volume is larger than the CCCO_2N 's. But the biomass carbon has in contrast to the commercial carbon nearly solely micropores and consequently has different adsorption properties as described in chapter 4.4.1.

The overall lower conversion of the esterification reaction might be explained by steric effects. Though the octanol is the larger molecule, it is not branched and therefore less

hindered for sterical reasons. The carbons active sites in their pores are more easily accessible for the octanol.

There are two potential explanations for the completely different results of the esterification reaction with hexanol. For this alcohol the best conversion result was achieved using the RFC1NS, which has, as a result of stronger acidic groups, by far the lowest value for the pH_{pzc} but only a similarly small total pore volume as the biomass carbon and the lowest microporous volume of all the ACs.

The first explanation for the great conversion of the hexanol reaction would be that the less acidic hexanol is more attracted to a due to the lower point of zero charge less positively charged surface.

The result could also simply be an outlier as well but since every reaction was only carried out once for a lack of time for repetitions this cannot be determined for sure at this point.

AC	pzc	Adsorption Isotherm			k ₁ [1/h]			Conversion at 8 h [%]		
		S _{BET} [m ² /g]	V _{total} [cm ³ /g]	V _{micro} [cm ³ /g]	Octanol	Hexanol	Isoamyl	Octanol	Hexanol	Isoamyl
NCN	3,98	1030	0.557	0.304	0.0209	0.0170	0.0144	68.17	62.36	58.24
RFC1N	3,27	552	0.280	0.155	0.0154	0.0112	0.0101	62.96	55.38	56.02
RFC1NS	2,88	552	0.280	0.155	0.0175	0.0190	0.0089	66.01	68.78	53.32
RFC2CO ₂ N	3,21	658	0.295	0.175	0.0167	0.0096	0.0090	63.84	52.04	53.45
CCCO ₂ N	3,58	630	0.251	0.214	0.0216	-	0.0173	69.42	-	68.10

Highest value

Second highest value

Third highest value

Lowest values

Table 8: Summary table for the catalysts' characteristic properties, kinetic parameter and conversion of the esterification reactions

5) Conclusion

The objective of this thesis was to prepare several types of carbon based heterogeneous catalysts and determine their suitability for the use as catalyst by the example of esterification reactions.

For this purpose a widely used commercial carbon was compared to a synthetic and a biomass carbon produced under laboratory conditions. The preparation of the synthetic carbon involved the fabrication of an organic polymer by sol gel method and its carbonization. Part of it was physically activated as well. Shredded corn cob was the feedstock for the biomass carbon, which was produced by pyrolysis and physical activation by a single thermal treatment.

These four types of activated then had to undergo a nitric acid and partly a sulfuric acid treatment in order to chemically alter their surface properties in terms of functional surface groups.

The procedure was then followed by the analysis of the ACs' chemical and physical properties determined by the estimation of the point of zero charge, elemental analysis and the record of a nitrogen adsorption isotherm at gas condensation temperature.

At last the catalysts were tested in three different esterification reactions, using the reactants acetic acid and octanol, hexanol or isoamyl alcohol, each.

It came out that the best results in terms of conversion of the reactions utilizing octanol and isoamyl alcohol are achieved by the catalysts with the highest points of zero charge and the largest microporous volume, whereby a large ratio of micropores to mesopores and the consequently differing adsorption properties seems to be more important than the absolute microporous void volume, since the conversion results of the biomass catalyst are, in spite of a smaller total void and microporous volume, even better than those of the commercial AC catalyst NCN. The production yields of these two carbons cannot be compared since the production yields accomplished by the manufacturer are not known.

The synthetic carbon catalysts' physical properties, such as total surface area, total, meso- and microporous volume, are mostly average or below average in comparison to the NCN and the CCCO₂N. The only special property is the low point of zero charge of the synthetic catalyst RFC2NS, which is also the only synthetic carbon that was

used in a reaction with high conversion results, which was an esterification reaction utilizing hexanol as a reactant. This carbon's production yield is with about 40 % more than twice as high as the biomass catalyst's however the preparation time of about two weeks needed for the production diminishes this advantage.

In summary the biomass carbon achieves the best catalytic results for most of the reactions, even though the commercial AC's results are almost as good. But additionally to the good catalytic results the CCCO_2N is made of a feedstock, which would otherwise be considered waste and so there are no further resources needed for the production, which makes this catalyst very environmentally friendly, especially in comparison to the RFC catalysts. Even though the RFC1NS was tested with good results in one reaction its production might not be profitable considering the expensive feedstock (pure chemicals) and the time consuming preparation, not to mention the live cycle assessment.

Therefore the biomass catalysts might be a suitable, environmentally friendly and alternative to the use of conventional homogeneous and heterogeneous catalysts.

6) Suggestions for Future Work

The research done in the course of this thesis was only a first step towards answering the question whether or not carbon based heterogeneous catalysts provide an alternative to conventional homogeneous and heterogeneous catalysts.

Due to a limited time frame it was only possible to produce a very small amount of the different catalysts and do a single determination of each analysis and reactions. Outliers are therefore hard to recognize as such. Hence the work should be verified in the future by repetition to check, if the results can be reproduced and enlarge the amount of data to make it more reliable. Results that are missing due to a lack of time in this thesis, such as the results of the NCNS catalyst and some results of the elemental analysis should be taken into account and compared to the other results as well.

Furthermore the reaction circumstances in terms of reaction temperature and educt concentration could be varied to find the ideal conditions for a fast with high conversion.

Alternatively the AC catalysts could be tested on suitability for the use in different reactions as well.

7) List of Abbreviations

AC	-	Activated carbon
CCCO ₂	-	Biomass carbon (corn cob)
CCCO ₂ N	-	Biomass carbon (nitric acid treatment)
GC	-	Gas Chromatography
NC	-	Norit carbon
NCN	-	Norit carbon (nitric acid treatment)
NCNS	-	Norit carbon (sulfuric acid treatment)
pzc	-	Point of Zero Charge
RFC1	-	Resorcinol formaldehyde carbon (batch 1)
RFC1N	-	Resorcinol formaldehyde carbon (nitric acid treatment)
RFC1NS	-	Resorcinol formaldehyde carbon (sulfuric acid treatment)
RFC2	-	Resorcinol formaldehyde carbon (batch 2)
RFC2CO ₂	-	RFC2 after activation with CO ₂
RFC2CO ₂ N	-	RFC2 after activation with CO ₂ (nitric acid treatment)
STP	-	Standard temperature and pressure
IUPAC	-	International Union of Pure and Applied Chemistry

8) Symbol directory

Symbols	Unit	Explanation
p/p°	-	relative pressure
n	mol	specific amount of gas adsorbed
n_m	mol/g	monolayer capacity
C	-	exponentially to the energy of monolayer adsorption related parameter [14]
S_{BET}	m^2/kg or m^2/g	specific surface area
A_m	$m^2/molecule$	area occupied by one molecule
N_A	$6.023 \times 10^{23}/(molecules\ mol)$	Avogadro number
r_1	mol/(l h)	Speed of reaction 1
r_2	mol/(l h)	Speed of reaction 2
C_A	mol/l	Concentration acetic acid
C_B	mol/l	Concentration alcohol
C_C	mol/l	Concentration ester
C_D	mol/l	Concentration water
T	h	Time
k_1	1/h	Reaction rate constant 1
k_2	1/h	Reaction rate constant 2
$C_{A,0}$	mol/l	Initial concentration acetic acid
$C_{B,0}$	mol/l	Initial concentration alcohol
dc_A	mol/l	Change in concentration of acetic acid
dc_B	mol/l	Change in concentration of alcohol
dt	h	Change in time
ΔC_A	mol/l	Numeric change in concentration of acetic acid
ΔC_B	mol/l	Numeric change in concentration of alcohol
Δt	h	Numeric change in time
α	mol/(l h)	$\Delta C_A / \Delta t$
β	mol/(l h)	$\Delta C_B / \Delta t$
$C_{A,new}$	mol/l	New numeric concentration of acetic acid
$C_{A,old}$	mol/l	Old numeric concentration of acetic acid

CB,new	mol/l	New numeric concentration of alcohol
CB,old	mol/l	Old numeric concentration of alcohol
CC,new	mol/l	New numeric concentration of ester
CC,old	mol/l	Old numeric concentration of ester

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11) List of Chemicals

Chemical	Concentration	Manufacturer
Acetic acid	99.7 %	Panreac
Acetone	99.5 %	Sigma-Aldrich
Formaldehyde	37-38 %	Panreac
Hexanol	98 %	MERCK
Isoamyl alcohol	98.5 %	Sigma-Aldrich
Nitric acid	65 %	Sigma-Aldrich
Octanol	99 %	MERCK-Schuchardt
Resorcinol	98 %	Aldrich
Sodium carbonate	99.5 %	Riedel
Sulfuric acid	95-97 %	Fluka
Undecane	99 %	SAFC

12) Appendix

12.1) Figures

12.1.1) Parity diagrams

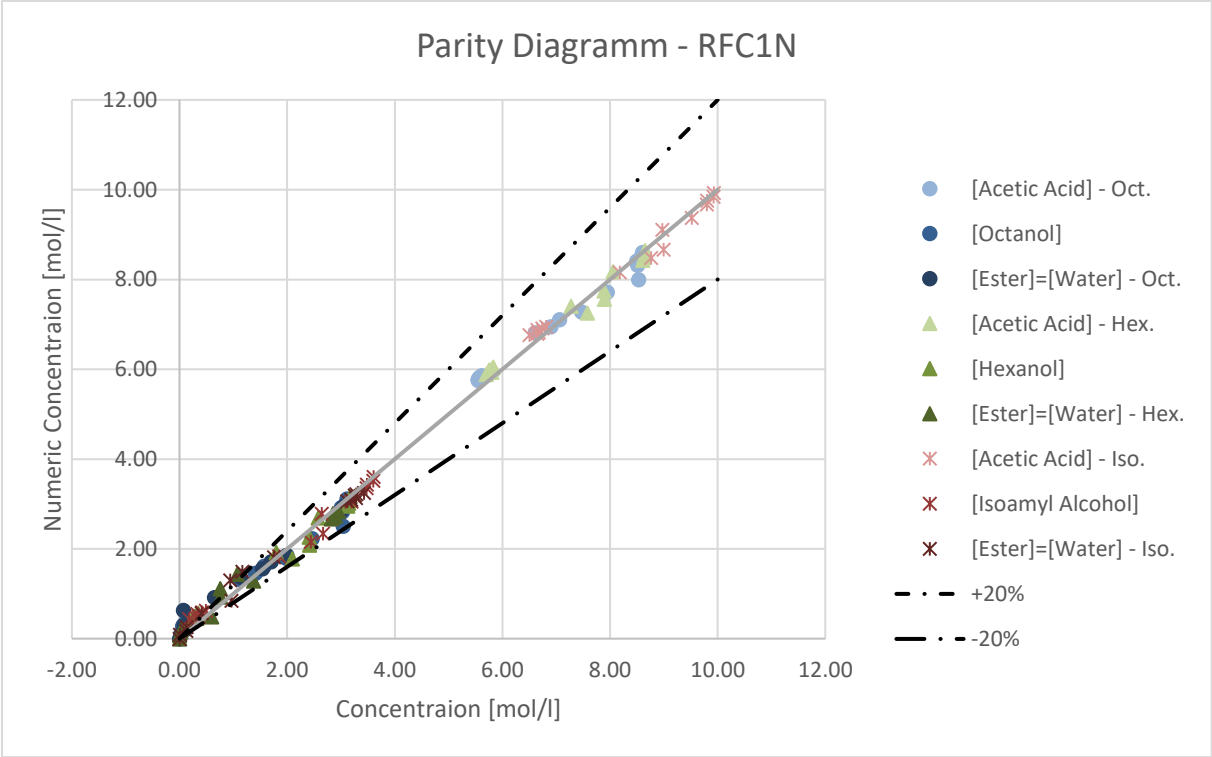


Figure 13: Parity diagram showing the relation of measured and numerically calculated concentrations for the reactions using RFC1N as catalyst

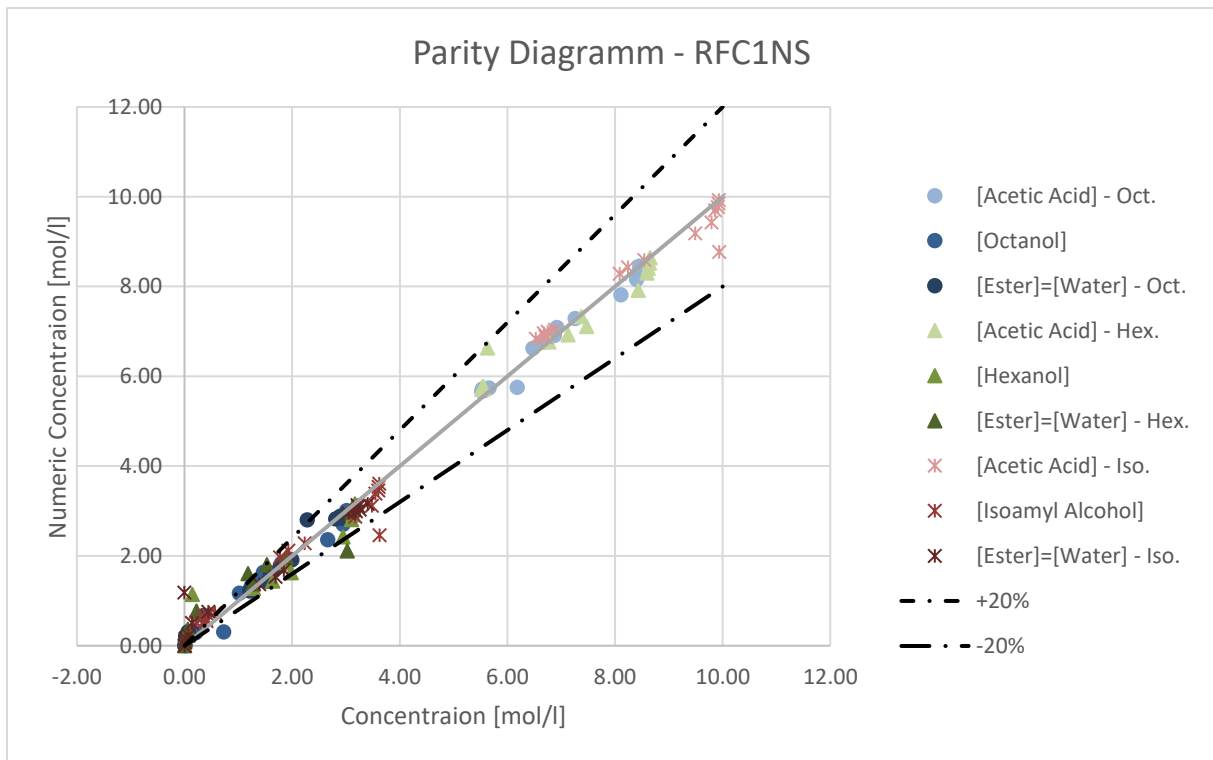


Figure 14: Parity diagram showing the relation of measured and numerically calculated concentrations for the reactions using RFC1NS as catalyst

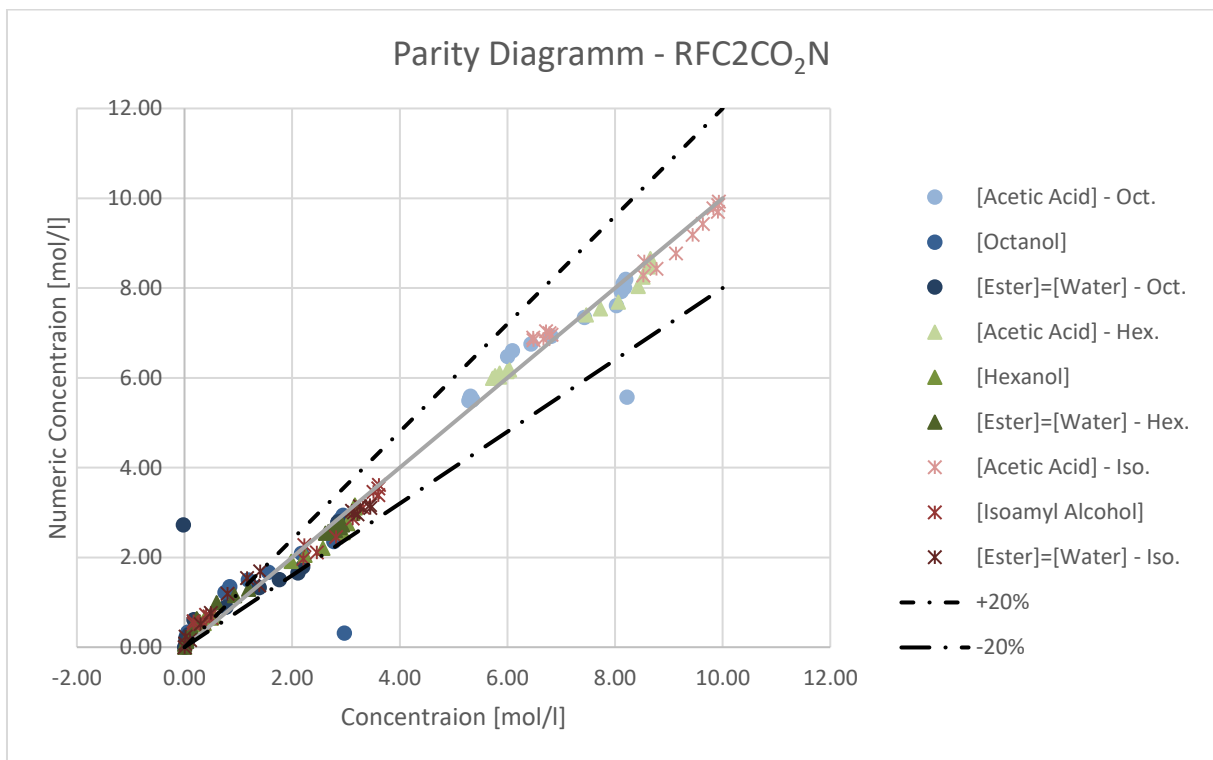


Figure 15: Parity diagram showing the relation of measured and numerically calculated concentrations for the reactions using RFC2CO₂N as catalyst

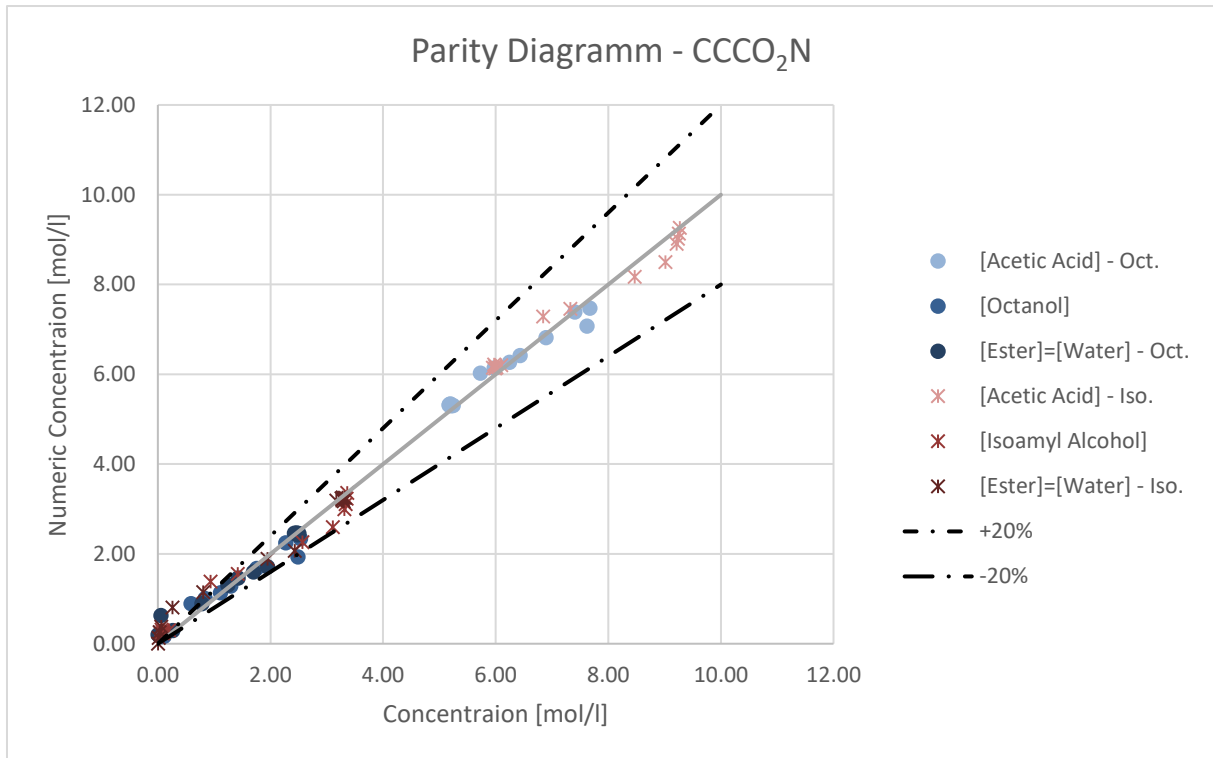


Figure 16: Parity diagram showing the relation of measured and numerically calculated concentrations for the reactions using CCCO₂N as catalyst

12.1.2) Adsorption Isotherms

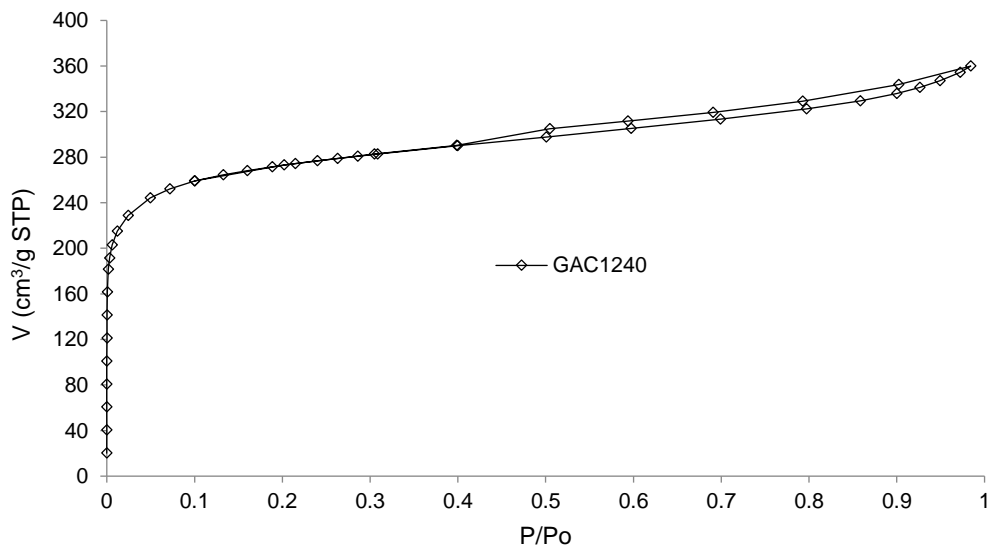


Figure 17: Adsorption isotherm NC

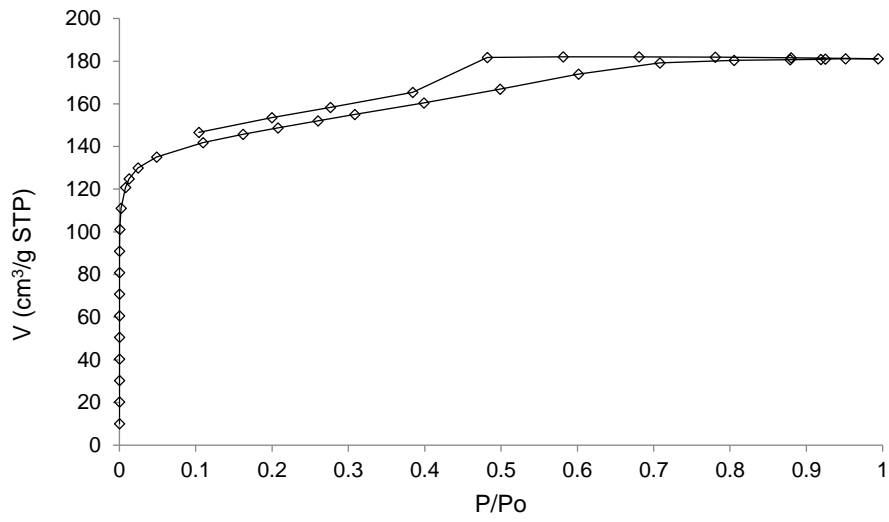


Figure 18: Adsorption isotherm RFC1

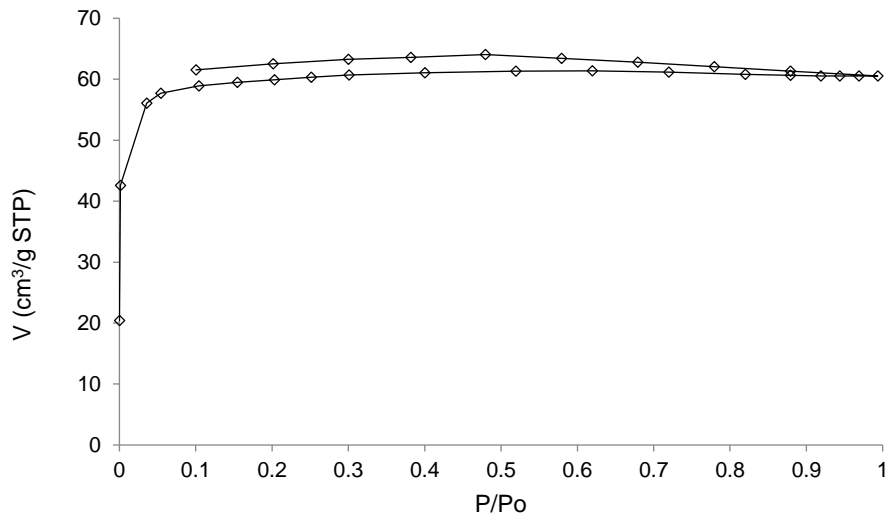


Figure 19: Adsorption isotherm RCF2

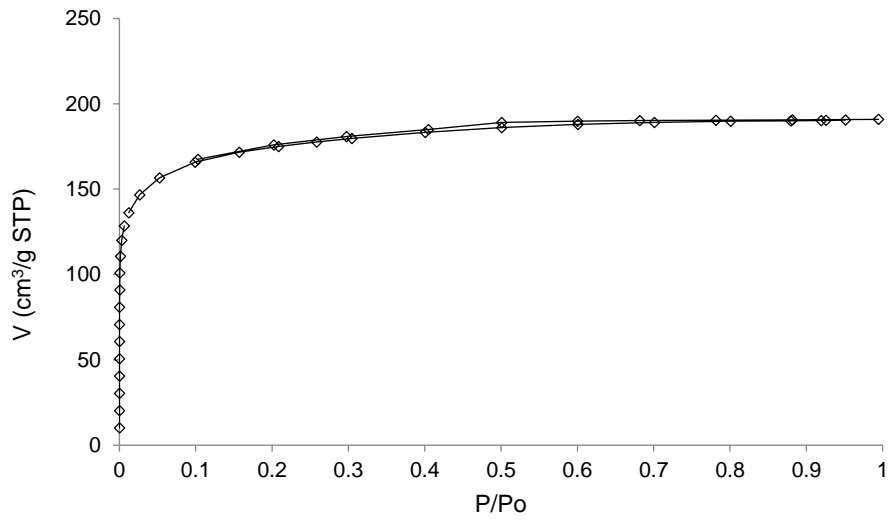


Figure 20: Adsorption isotherm RFC2CO₂

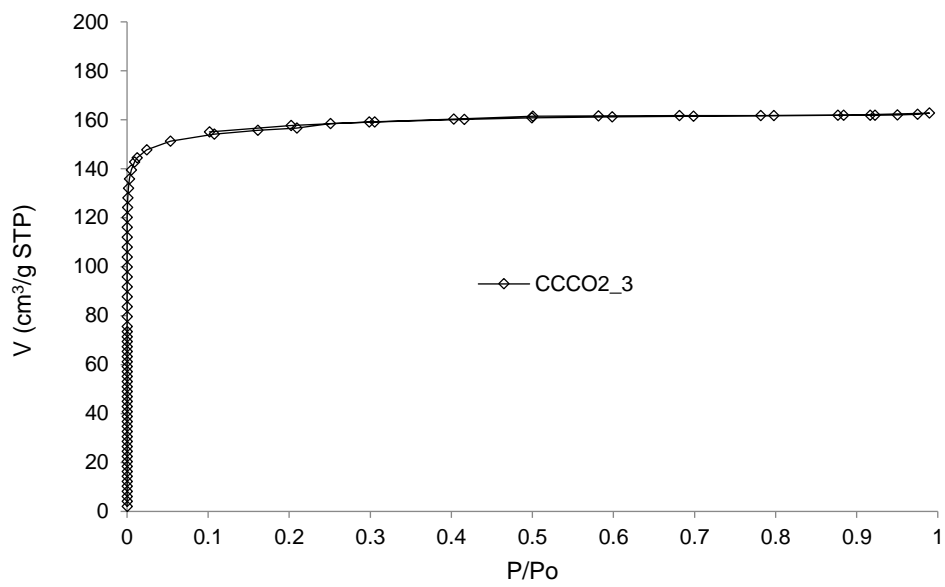


Figure 21: Adsorption isotherm CCCO₂

12.2) Tables

Step	Carbons	Mass input [g]	Mass output [g]	Yield [%]
Nitric acid treatment Sulfuric acid treatment	NC	10.00		
	NCN	10.00	10.00	99.95
	NCNS	4.00	3.99	99.79
Carbonization	RFC1	14.00	7.56	53.97
Nitric acid treatment	RFC1N	7.56	7.19	95.16
Sulfuric acid treatment	RFC1NS	3.60	2.94	81.51
Carbonization	RFC2	14.33	4.00	27.94
Activation	RFC2CO2	4.00	2.61	65.28
Carbonization + activation	RFC2CO2			18.24
Nitric acid treatment	RFC2CO2N	2.61	2.06	78.77
Carbonization + activation	CCCO2_1	6.00	1.50	24.98
Carbonization + activation	CCCO2_2	6.00	1.35	22.53
Carbonization + activation	CCCO2_3	6.03	1.22	20.18
Carbonization + activation	CCCO2_4	6.01	0.00	0.00
Carbonization + activation	CCCO2_5	6.01	1.25	20.87
Carbonization + activation	CCCO2_6	6.00	0.88	14.57
Carbonization + activation	CCCO2	18.03	3.34	18.54
Nitric acid treatment	CCCO2N	3.04	2.77	91.14

Table 9: Yields of every step during the carbon preparation process

13) References

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