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Alumina-Silica Impregnation in Biochar for Catalytic
Cracking.

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Cracking.

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RESUMEN

En el presente estudio, se impregnó catalizador de aluminosilicato (Al/Si) en una matriz de biochar activado de espigas de arroz y se lo probó para el craqueo catalítico de aceite de motor usado. Se realizó una investigación cinética, a la par de una caracterización de los materiales y los productos.

Para las reacciones de craqueo térmico y catalítico, se siguieron métodos utilizados en previas contribuciones de nuestro equipo. En estos trabajos se demostró que, la velocidad de reacción incrementa al usar catalizadores Al/Si y Al/Si con adición de Zn. Se sintetizó el biochar vía pirólisis utilizando un reactor horizontal con atmosfera inerte. La activación del biochar fue necesario para incrementar porosidad, y a su vez, adsorción. Se hizo uso de una solución de KOH 3M para el proceso de activación. Interesantemente, el biochar activado demostró mayor actividad comparado con el catalizador de base Al/Si para craqueo catalítico de aceite de motor usado (0.0176 [1/min] para biochar activado; 0.0068 [1/min] para catalizador Al/Si).

Con la finalidad de incrementar la actividad del biochar activado, la impregnación Al/Si en una matriz de biochar fue estudiada. Dos materiales fueron sintetizados. 30 y 100 wt% de Triton X-114 (surfactante) fue sustituido con biochar antes de la impregnación de Al y Si. Ambos materiales fueron examinados en el reciclaje de aceite de motor usado. En contraste a lo esperado, el procedimiento de impregnación redujo o mantuvo la actividad de la matriz de biochar. Por la caracterización del catalizador se concluyó que, después de la calcinación de los materiales, biochar pierde sus propiedades con la formación de cenizas. Por lo tanto, existe la posibilidad de que la porosidad y las propiedades superficiales fueron alteradas.

Finalmente, el producto final de la reacción de craqueo catalítico fue caracterizado con un cromatógrafo de gases acoplado a espectrometría de masas (GC-MS). La dispersión en el espectro es similar al del diesel comercial, lo cual lo convierte en la materia prima perfecta para la síntesis de combustibles tipo diesel. La viscosidad del producto es de $2.76 \text{ m}^2\text{s}^{-1}$, lo cual sigue los requerimientos para diesel #2 según NTE INEN 810.

Palabras clave: catalizador, biochar, pirólisis, craqueo, porosidad, actividad, conversión.

ABSTRACT

In the present study, Al/Si catalysts were impregnated into an activated rice husk biochar matrix and tested for the catalytic cracking of waste motor oil. A kinetic investigation, materials and reactions products characterization were also developed.

Firstly, thermal and catalytic reactions, following the method used in a previous contribution of our group, were developed. There, reaction rate increment when using Al/Si catalyst and Al/Si doped with Zn was demonstrated. Then, biochar via pyrolysis in a horizontal reactor and inert atmosphere was synthesized. Activation of biochar was needed in order to increase porosity, thus, adsorption. A KOH 3M solution was used for the activation process. Interestingly, activated biochar showed a much better activity compared to Al/Si based catalyst for the catalytic cracking of waste motor oil (0.0176 [1/min] for activated biochar; 0.0068 [1/min] for Al/Si catalyst).

In order to increase the biochar activity, Al/Si impregnation under the biochar matrix was studied. Two materials were synthesized. 30 and 100 wt.% of Triton X-114 (surfactant) was substituted with biochar before Al and Si impregnation. Both materials were screened in waste motor oil recycling. In contrast to what it was expected, the impregnation procedure diminished or kept the activity of the biochar matrix. From catalyst characterization, after materials calcination, biochar seems to lose their properties with the formation of ashes. Thus, the author belief, porosity and surface properties were changed.

Finally, the final product of the catalytic cracking reaction was characterized with a gas chromatography-mass spectroscopy (GC-MS). The dispersion in the spectrum is similar to commercial diesel, which makes it a perfect raw material for the synthesis of a diesel-like fuel. Viscosity of the product is $2.76 \text{ m}^2\text{s}^{-1}$, which follows the requirements of NTE INEN 810 for diesel #2.

Key words: catalyst, biochar, pyrolysis, cracking, porosity, activity, conversion.

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I. Introduction

For centuries, humans have been using coal, oil, and gas as a resource to provide more than 70 percent of their energy needs[1]. In modern society, fossil fuels are the main source of energy to power cars, businesses, and industries. The constant use of these fuels has taken a big toll on the environment and humanity. Land degradation, water pollution, and benzene emissions are just a fraction of the impact of the extended use of this type of fuels[2]. Particularly, the use of cars, as a means of transportation, has dramatically increased during the years, hence, the use of motor oils represents a huge percentage on the fossil fuels impact.

There are several processes to recycle waste motor oil (WMO) in literature. Distillation, clay treatment, acidic refining and hydrogenation are some of the techniques used[3]. Among other recycling technologies, thermal cracking reaction offers a sustainable and feasible way to reuse of waste motor oil[4]. This reaction reuses the oil to produce a resource for the synthesis of diesel-like fuels. The process can be improved by the presence of a catalyst, as shown by Vargas et al[5]. There, three different catalysts were used catalytic cracking to compare to the thermal cracking reaction. The results showed that the overall yield of the reaction increased from 63 to 90% in the presence of Al/Si matrix with 2% zinc. Also, the kinetic study showed that the activation energies for the catalytic conversion were lower, being the lowest value the one with Al/Si matrix with 2% zinc (287.37 kJ/mol). The final product obtained by all the different cracking processes meet the necessary requirements for diesel #2.

Biochar is a material derived from a variety of waste biomass. It is a low-cost carbon-rich material. It can be synthesized via pyrolysis with a low percentage of oxygen or hydrothermal carbonization under high pressure[6]. Due to its stability, enriched surface functional, and high pore volume, biochar has a large variety of applications[7]. It can increase nutrient interaction in soil, suppress greenhouse gas emissions by carbon sequestration, immobilize contaminants through precipitation for soil remediation, and remove organic chemicals and heavy metals on wastewater treatments[8]. Due to its large surface area, biochar applications can be redirected towards biochar-based catalyst for biorefinery[9].

Biochar can be used as a heterogeneous catalyst by itself, but it must be activated first. The activation process is done to modify the biochar internally and morphologically.

Before activation, the tendency of adsorption or absorption is low. Clogged pores, insignificant pore size, breakage of bonds between organic components, less surface area distribution, and reduction of pore size and volume by contaminants are some of the downfalls of an improper activation treatment[10]. There are two categories of activation techniques: chemical and physical. Physical activation requires a flow of gas agents CO₂ steam at a temperature of 700 °C[11]. Chemical activation requires an activator (KOH, H₃PO₄, H₂O₂, ZnCl₂, potassium carbonate) added during the carbonization phase. In order to enhance the degree of adsorption, the activating agent must have a high potential of adsorption. The degree of adsorption depends on the adsorbate and the adsorbent. The activation that is employed on this investigation is an activation by KOH, which increases the surface area by 1.8 m²/g and the total volume of the pores by 8.73 mL/g[12].

Previous investigations had shown that the addition of rice husk in aluminum alloy matrix yields better physical and mechanical properties and high wear rate resistance of composite[13]. The synthesis of an aluminum-silicate biochar-based catalyst would solve the above-mentioned problem of Al/Si since it can withstand high temperatures without consuming. Additionally, it would improve the aluminum silicate's yield.

This investigation focuses on the impregnation of aluminum-silicate catalyst into rice husks biochar for the catalytic cracking of WMO. The advantages of the presence of a biochar matrix are discussed via a kinetic study. Moreover, products and catalyst are characterized for discussion.

II. Methodology

II.I Reagents

The reagents used for the synthesis of the aluminum silicate catalysts are Triton X-114 (laboratory grade), tetraethyl orthosilicate (TEOS, 98% purity), aluminum tri-sec-butylate (TBA, 97% purity), concentrated nitric acid (HNO₃), zinc chloride dry (ZnCl₂, 98% purity) and ethanol 99%. For the biochar activation, potassium chloride (KOH) 3 M was used. The waste motor oil was supplied by a collection station in Quito.

II.II Cracking Process

The motor oil recovered must undergo a pretreatment phase before the cracking reaction. The oil was stirred and heated to 100 °C for 2 hours and then sifted to remove any solid or water residue. For the cracking reaction, 40 mL of waste motor oil is poured in a 250 mL temperature-resistant flask. For catalytic cracking, 0.04 wt% of catalyst is added. A Precision Scientific Petroleum Herzog equipment was filled with water at 40-60 °C. The equipment must be preheated for 10 minutes at 50% power[5]. The flask is inserted in the heater section of the equipment, where the cracking reaction vapor will be condensed. The equipment is then set to 85% power. The temperature of the oil and volume of recovered oil was measured throughout the reaction every 5 minutes for 3 hours. A gas sampling bag was used for collecting gas product from the reaction. A graduated cylinder was used to recover de condensate.

II.III Kinetic Study

The kinetic constant for every cracking reaction was calculated by using the following equation:

$$-\ln\left(\frac{M_A}{M_{A0}}\right) \quad (1)$$

Where M_A is the initial mass of the WMO decreasing throughout the reaction, and M_{A0} is the WMO initial mass. M_A was calculated by using this expression:

$$M_A = M_{A0} - m_{condensate} - m_{gas} \quad (2)$$

Where $m_{condensate}$ is the mass of the condensate accumulating throughout the reaction, and m_{gas} is the increasing mass of the gas product. m_{gas} was calculated using the relationship between the total mass of condensate ($Tm_{condensate}$) and the total mass of gas produced (Tm_{gas}):

$$m_{gas} = \frac{Tm_{condensate}}{Tm_{gas}} \quad (3)$$

The slope formula of the equation (1) vs time shows is then calculated, where the slope is the kinetic constant of the reaction.

II.IV Biochar Synthesis and Treatment

The rice husks must undergo a pretreatment phase before pyrolysis. It was heated to 60 °C in an oven for 48 hours to remove any water residue. Dry rice husks were then relocated into a horizontal pyrolysis reactor at 700 °C with a 5 °C/min ramp and 1 hour of dwell[14]. The resulting biochar was then activated. For this phase, C. Zhao et al. method was used[15]. The biochar was mixed with KOH 3M and stirred at 600 rpm and heated at 70 °C for 2 hours. The biochar was then filtered and washed with distilled water till it's pH decreased till neutral. The activated carbon was dried overnight in an oven at 105 °C.

II.V Aluminum-Silicate and Impregnated Catalyst Synthesis

M. Ruales and S. Corella method was used for the synthesis of aluminum-silicates[5]. Triton X-114 is stirred with distilled water and 2% ZnCl₂ dry. HNO₃ is then used to decrease the pH to 1. TEOS is added in a continuous drip. The mixture is then stirred for 2 hours before adding TBA. After 20 hours of stirring, the resulting mixture is transferred to an oven for 24 hours at 150 °C. The solid mixture is then washed with ethanol 50%. Finally, the dry product is calcined at 550 °C for 24 hours. The final product pulverized and sifted in a 120-mesh sieve.

For the impregnation process, Triton X-114 was replaced for activated biochar. One batch of 70% biochar and 30% Triton X-114, and another with 100% biochar. The calcined time was reduced to 2 hours.

Table 1: Synthesized materials in this work

Name	Matrix	Impregnation
Si/Al	Si/Al	-
Si/Al+2Zn	Si/Al	2Wt% Zn
Biochar	Rice husks	Basic treatment
Impregnated Catalyst 70%	Rice husks (70wt%) + Triton X-14 (30wt%)	AL/Si
Impregnated Catalyst 100%	Rice husks	AL/Si

II.VI Characterization

The final product of the catalytic cracking reaction was characterized using a Shimadzu gas chromatography-mass spectroscopy (GC-MS) model QP2010 Ultra Plus to identify the carbon number of the liquid products. 0.5 mL of sample were diluted by 2.5 mL of diethyl ether and left to refrigerate for 40 minutes before injection. The oven began at a constant temperature of 50 °C for 1 minute. Then, the oven was set to 280 °C with 4 °C/min ramp and 10 minutes of dwell. The injector temperature was 320 °C, 1.2 mL/min helium flow rate, 5 mL/min purge flow, and 100 mL/min split flow. The MS transfer was set to 320 °C, and the ion source to 230 °C[16]. Viscosity of the condensate was measured using an Ostwald Zeitfuchs viscometer at 40 °C. Flashpoint and density were determined as well.

The catalysts were characterized for imaging and analysis by Scanning Electron Microscope (SEM), and Agilent Technologies Fourier-transform infrared spectroscopy (FTIR) Carry 630. For the SEM, a Tescan Mira 3 microscope with a Schottky Field Emission Gun (Schottky FEG-SEM) was used for the morphological analysis. The samples were fixed on SEM stubs and covered with a 20 nm gold layer (99.99% purity) employing a sputtering evaporator Quorum Q150R ES. An Energy Dispersive Spectroscopy (EDS) was used for the elemental analysis on the SEM chamber at 30 kV with a Bruker X-Flash 6|30 detector. The samples were fixed in a stub and double coated with layers of carbon conductive tape.

III. Results and Discussions

III.I Cracking Results

The temperature for every cracking reaction stabilized at 405-420 °C, after a 15-minute stabilization period, as shown in **Figure 1** (blue curve). Once the temperature is stabilized, the condensate started to accumulate, as also shown in **Figure 1** (gray curve).

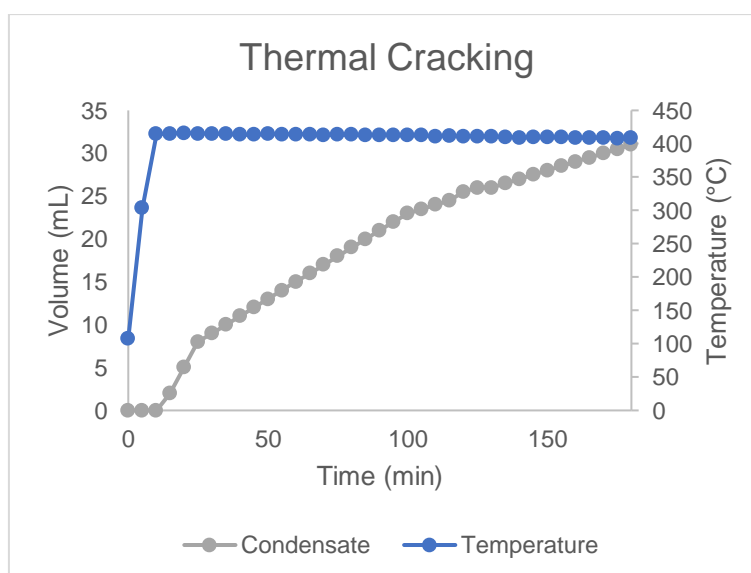


Figure 1: Volume of condensate and temperature during the reaction for thermal cracking.

The WMO mass decrease throughout a 150-minute reaction after stabilization period is presented in **Figure 2 (left)**. Thermal and catalytic reactions for Si/Al catalysts reached a minimum of 16 grams, 7 grams for the 70% impregnated catalyst and 3 grams for biochar and 100% impregnated catalyst. It means, biochar-based catalyst shows a higher conversion, as shown in **Figure 2 (right)**. Catalytic cracking with biochar and impregnated catalysts shows a conversion of 90%, 79% and 76% for Al/Si and Al/Si + Zn 2% catalysts, respectively, and 61% for thermal cracking. Thus, biochar alone, seems to develop the higher conversions.

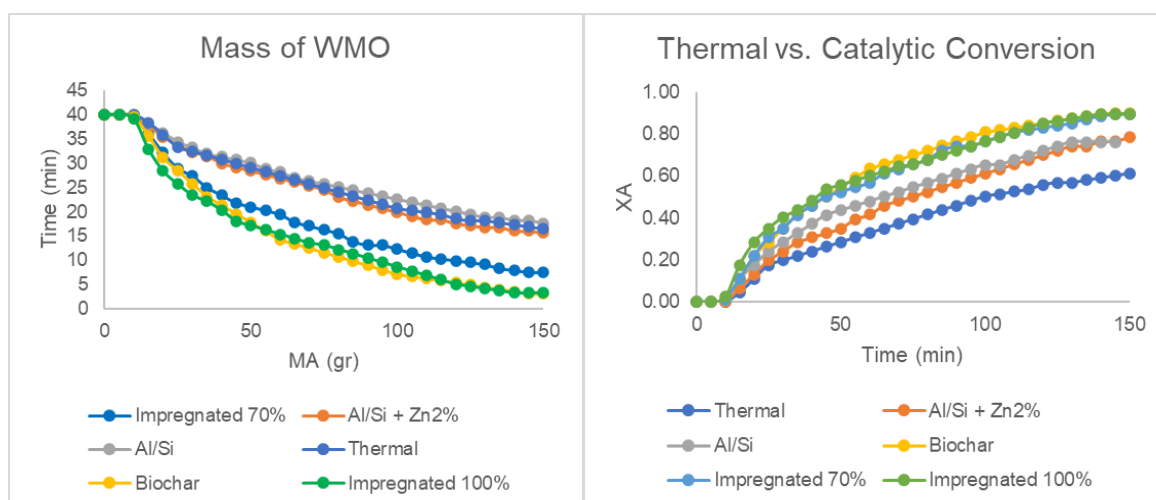


Figure 2: Mass of WMO converted (left) and conversion (right) throughout the cracking reaction

III.II Kinetic Results

For further understanding, kinetic constants were calculated for all catalytic and thermal cracking reaction utilizing **Equation 1**. **Table 2** shows each constant for every reaction. Firstly, all the reactions have been proven to be pseudo first-order (see **Figure A6** – **Figure A11**), which means that the reaction rate is linearly dependent on the concentration of the WMO. Al/Si and Al/Si Zinc 2% show a better activity compared to the thermal cracking, in accordance with Vargas et al. [5]. Interestingly, biochar with basic treatment, increased considerably the speed of reaction. However, from the results, it seems that the impregnation method for Al/Si together with biochar does not give a better activity. As the kinetic constant for biochar and impregnated catalyst 100% are statistically equal. (**Figure 3**). Some insights for these behaviors can be elucidated in the following characterization section.

Table 2: Kinetic constants for all cracking reactions

Reaction	k (1/min)
Thermal	$0.0057 \pm 2.45E-03$
Al/Si Catalyst	$0.0068 \pm 4.32E-03$
Al/Si + Zn 2%	$0.0083 \pm 4.19E-03$
Biochar	$0.0176 \pm 5.68E-03$
Impregnated Catalyst 70%	$0.0161 \pm 7.13E-03$

Impregnated Catalyst 100%	$0.0180 \pm 6.03E-03$
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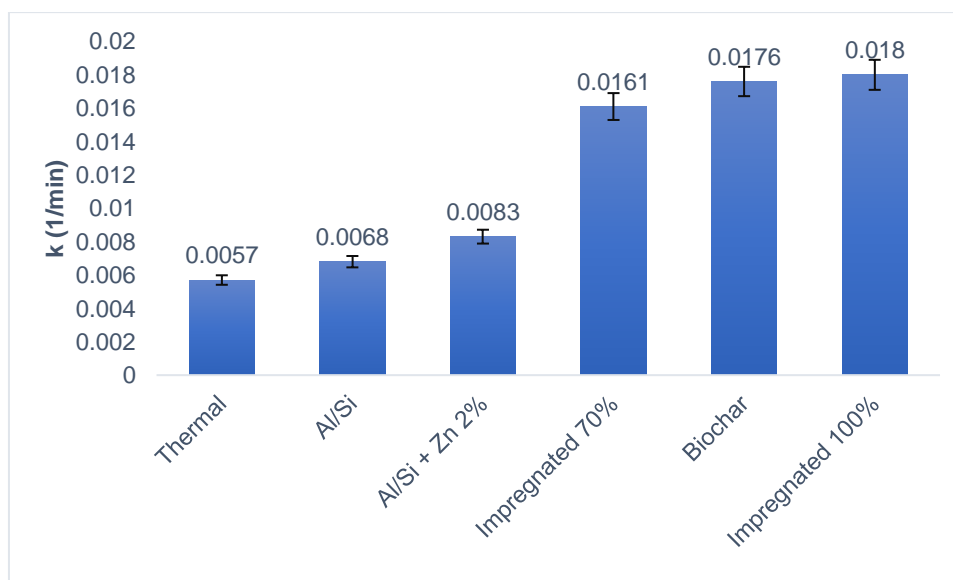


Figure 3: Kinetic constants for the different cracking reactions.

III.II Characterization Results

SEM and EDS analysis were performed for the Al/Si and Al/Si + Zn 2% catalysts, the activated and non-activated rice husk biochar. Sadly, no SEM and EDS analysis were performed for impregnated catalyst, due to the timeline for this work.

As shown in **Figure 4** and **Figure 5**, the Al/Si catalyst were successfully replicated from Vargas et. al [5]. As expected, they show a typical pore structure for silica-alumina sample. Moreover, from EDS, the major components of the catalytic system were Al and Si. For Al/Si impregnated with Zn, similar morphology was observed, but the EDS spectrum clearly show the presence of Zn, which is related to the better activity of the catalyst.

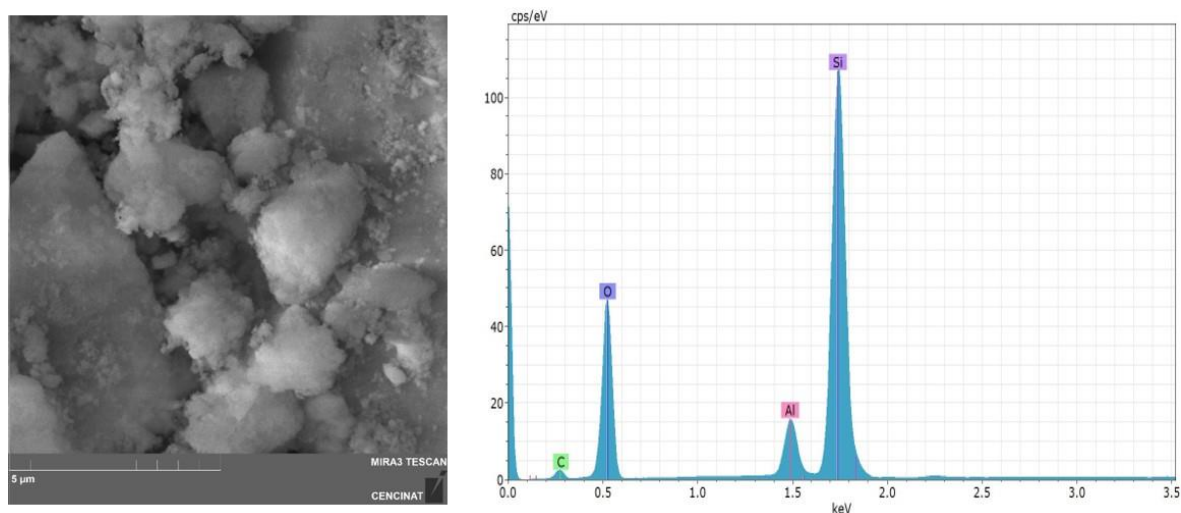


Figure 4: SEM imagen (left) and EDS spectrum (right) of the Al/Si catalyst

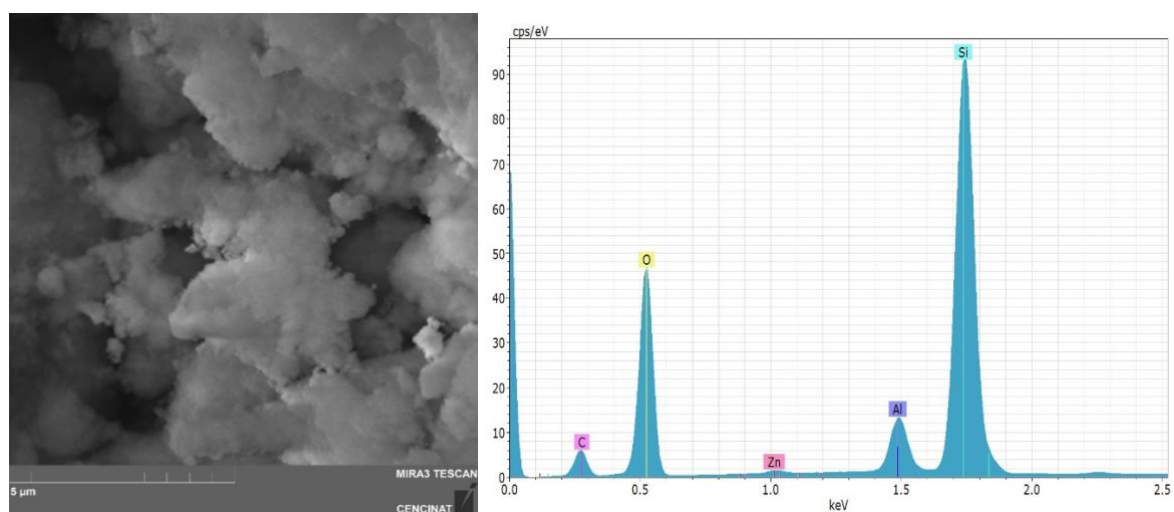


Figure 5: SEM imagen (left) and EDS spectrum (right) of the Al/Si + Zn 2% catalyst

Activated rice husks biochar showed a significant increase on the number of pores with wider volume than rice husk biochar (**Figure 6**). This translates into a higher degree of adsorption, which enhances the capturing of the desirable material and improves the quality of the biofuel produced and the speed of reaction [10].

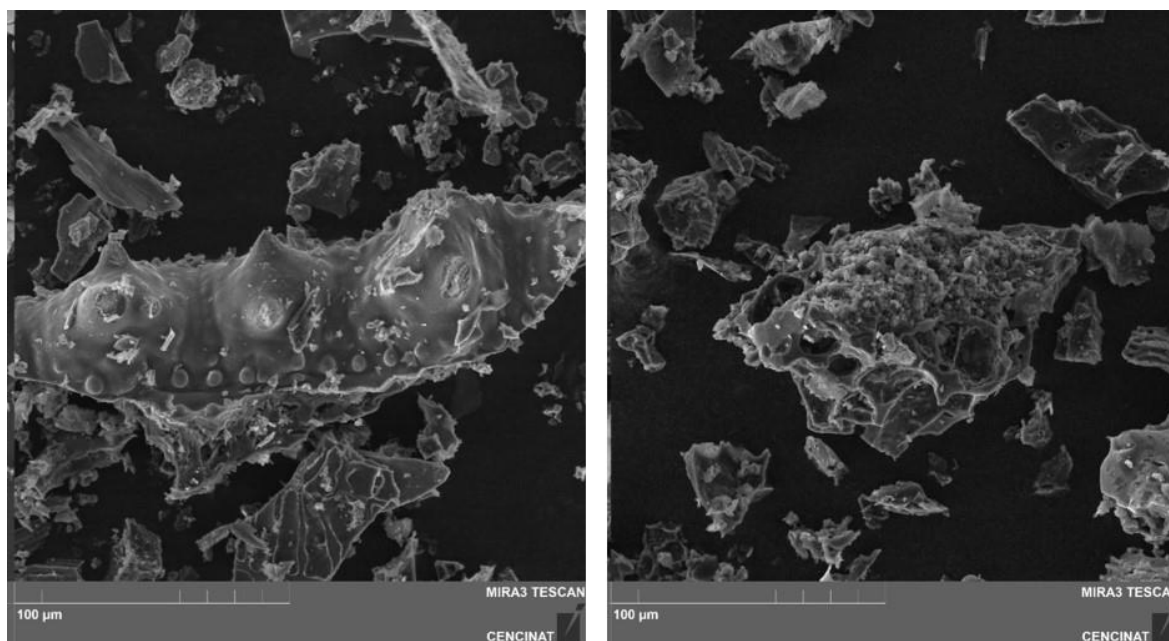


Figure 6: SEM image for the rice husk biochar (left) and for the activated rice husk biochar (right)

For further understanding, FTIR spectra of the various catalysts and the rice husk biochar are presented in **Figure 7**. For AL/Si based catalysts, bands at above 3600 and 1640 cm^{-1} correspond to -OH groups of water that are present on the surface of the catalysts. The peaks at around 870 and 1400 cm^{-1} are attributed to CO_3^{2-} group. This is due to the CO_2 in the air that reacted with the alkali during synthesis[15]. The absorption vibration peak near 1050 cm^{-1} is attributed to the Si-O-Si group, due to the high percentage of Si material present in the catalysts[17].

However, biochar impregnated catalyst showed almost the same spectra than AL/Si catalyst. This comes from the presence of Si in the impregnation procedure, but also for the transformation of biochar into ashes during the calcination process. In order to synthesize any AL/Si catalyst, a calcination process is necessary to evaporate any excess reagents. Since 90% of rice husk ashes are Si, a full silica material is obtained. Then, the lower activity of impregnated materials can be understood, as the biochar porosity can be degraded during catalyst calcination[18].

Since biochar contains Si, the peak for Si-O-Si is more pronounced for the 100% impregnated catalyst.

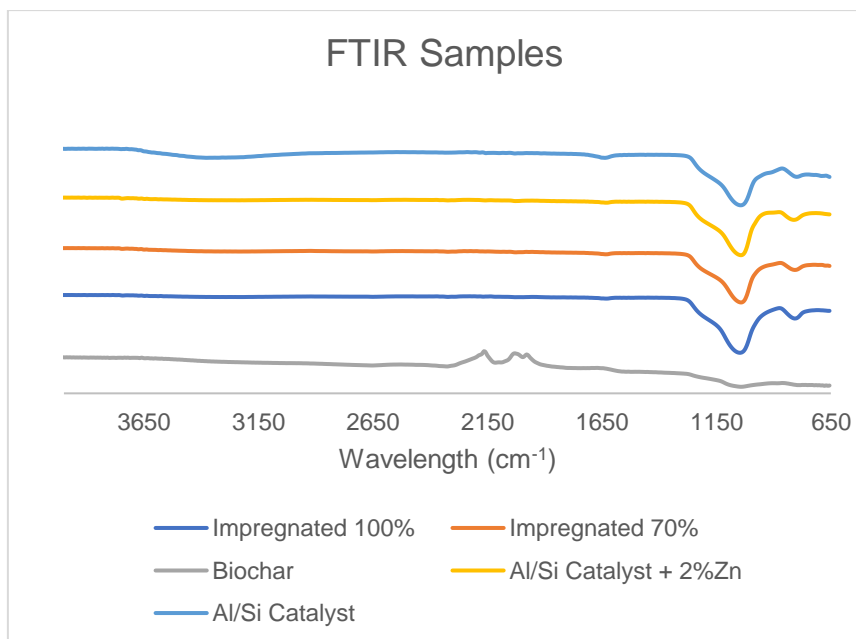


Figure 7: FTIR graphs for all different catalysts and for the activated biochar.

In the calcination phase, for the impregnated catalyst synthesis, the sample was in contact with oxygen while heated. This resulted in a catalyst impregnated with biochar ashes. Ash-based catalysts are not only renewable and environmentally friendly, but they also show good catalytic performance to produce biodiesel, which is why the yield still increased [18]. Nonetheless, this may have affected the morphology of the activated biochar, which can implicate reduction of the porosity. This affects yield percentage and activity.

The product condensate of the catalytic reaction with the 100% impregnated catalyst was analyzed by GC-MS and compared to chromatograms of commercial diesel. The product of catalytic cracking (**Figure 9**) shows a broad spectrum of compounds from C₁₁ till C₃₀ in a similar range as in the diesel chromatogram (**Figure 8**) but with a higher intensity of heavy materials. Catalytic product shows a narrow range of peaks between C₈ and C₁₃, which results in light hydrocarbons that range like gasoline [5]. The viscosity of the condensate, shown in (**Table A1**), is 2.76 m²s⁻¹, the range of viscosity required for diesel #2 is 2.5-6.0 m²s⁻¹ according to INEN 810.

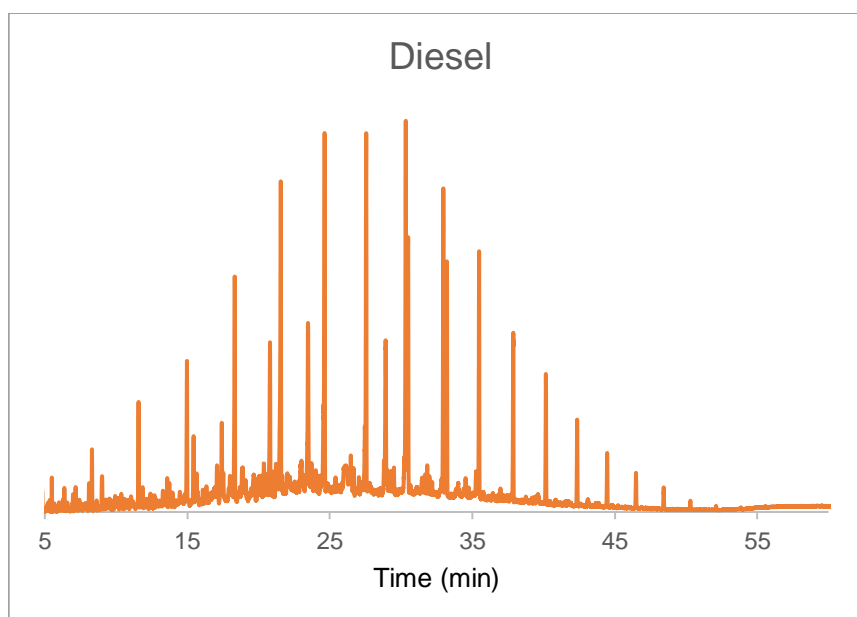


Figure 8: Chromatogram by GC-MS of commercial diesel

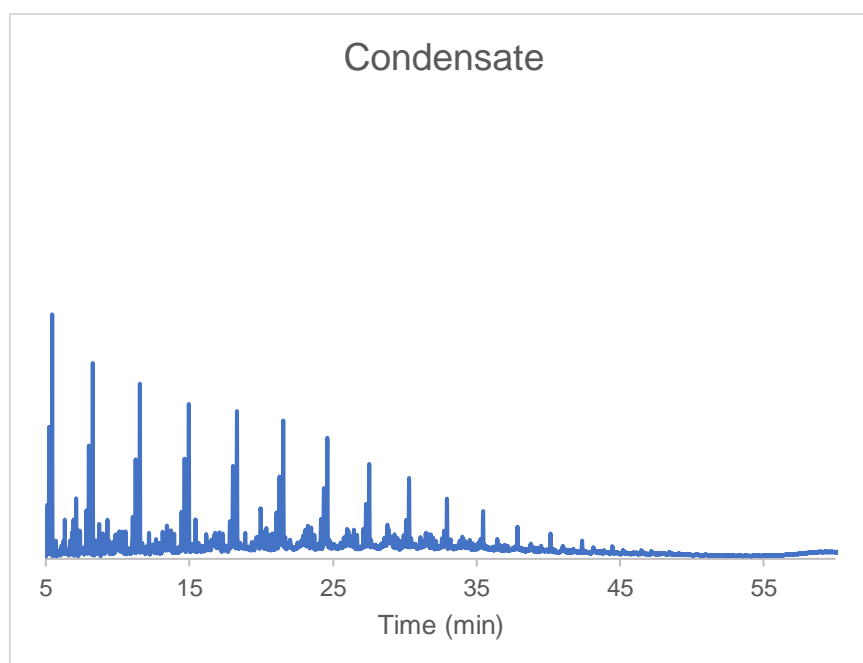


Figure 9: Chromatogram by GC-MS of the reaction condensate

IV. Conclusion

Biochar showed an overall high conversion and activity for catalytic cracking compared to thermal and Al/Si assisted reactions. However, biochar impregnation with Al/Si did not show a catalytic increment. There are no differences between the Al/Si and the impregnated catalysts in the FTIR analysis. This shows that all the biochar components were lost during synthesis. Calcination phase turned the biochar into ashes, which may affect it's

morphology by cluttering or decreasing biochar porosity. This results in a reduction of adsorption degree.

The condensate product of catalytic cracking has a similar dispersion of carbon groups to commercial diesel, which makes it great raw material for the synthesis of a diesel-like fuel. The viscosity also relies into the INEN values for diesel #2

Since the calcination process tampered with the morphology of biochar, because of the presence of oxygen, an alternative might be impregnate raw biomass prior the pyrolysis procedure. Moreover, as the addition of Zn improved the Al/Si activity, might be interesting to impregnate biochar with different metals for improving its activity.

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VI. Appendix

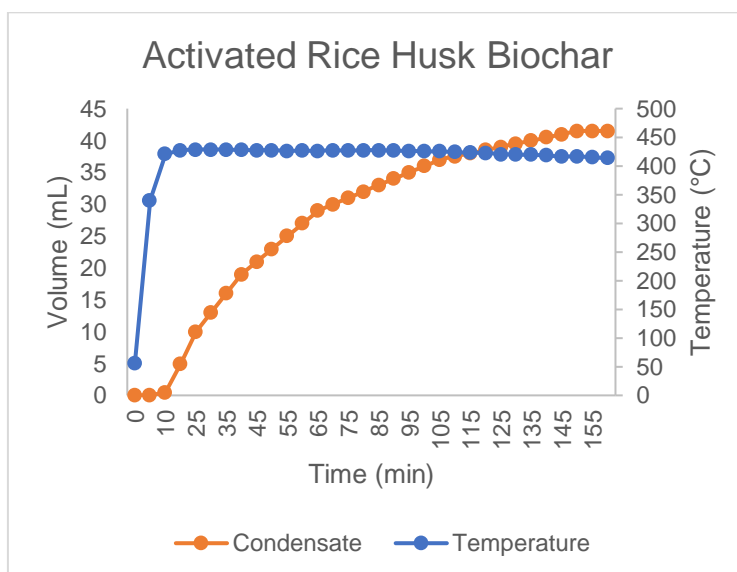


Figure A 1: Volume of condensate and temperature during the reaction for catalytic cracking (Biochar).

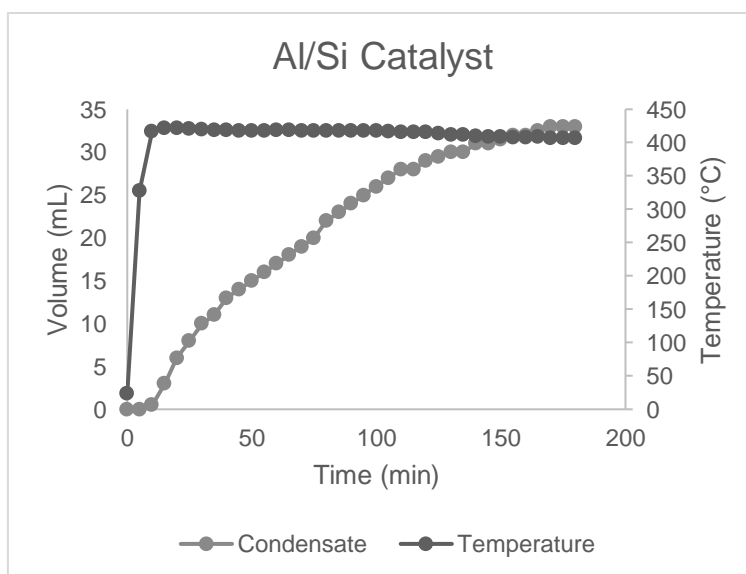


Figure A 2: Volume of condensate and temperature during the reaction for catalytic cracking (Al/Si).

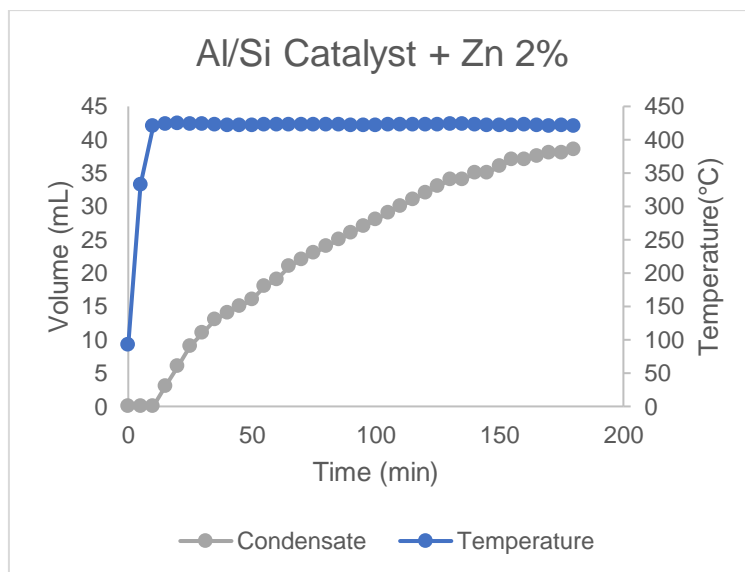


Figure A 3: Volume of condensate and temperature during the reaction for catalytic cracking (Al/Si + Zn 2%).

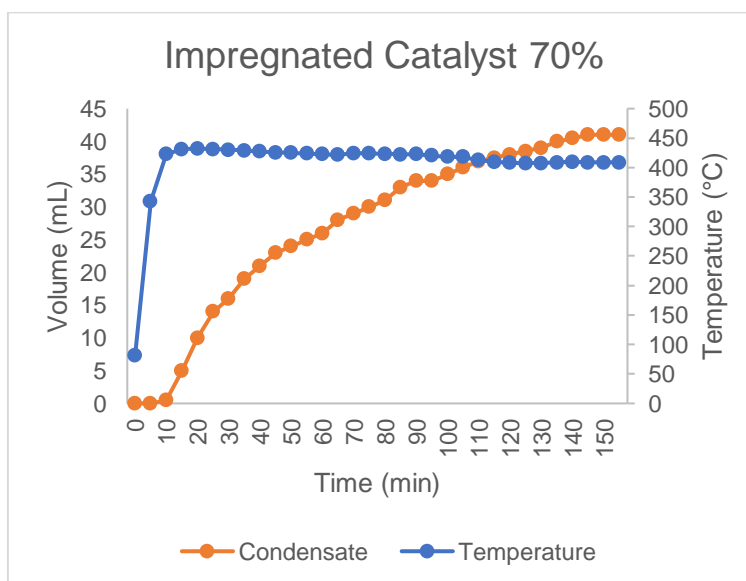


Figure A 4: Volume of condensate and temperature during the reaction for catalytic cracking (Impregnated 70%).

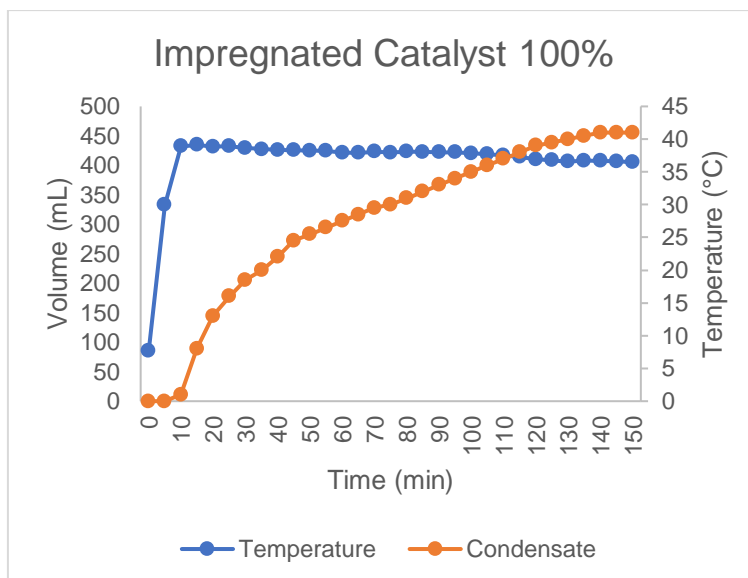


Figure A 5: Volume of condensate and temperature during the reaction for catalytic cracking (Impregnated 100%).

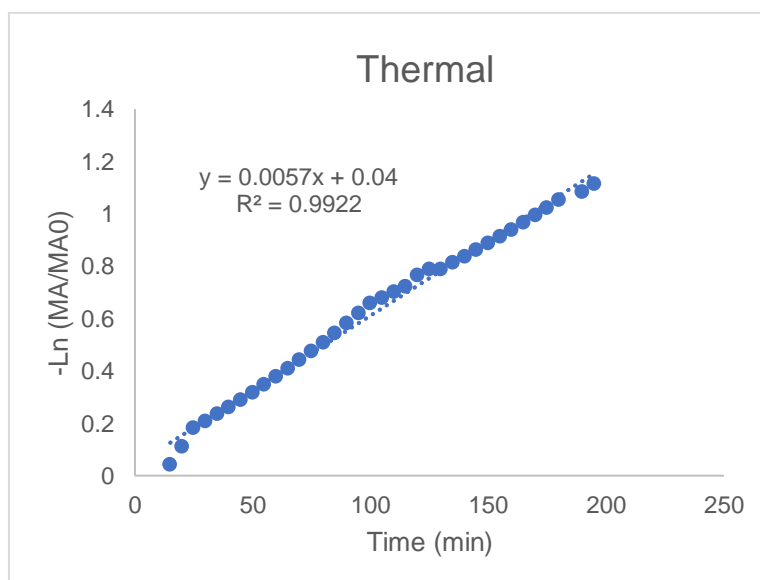


Figure A 6: Kinetic constant for thermal cracking

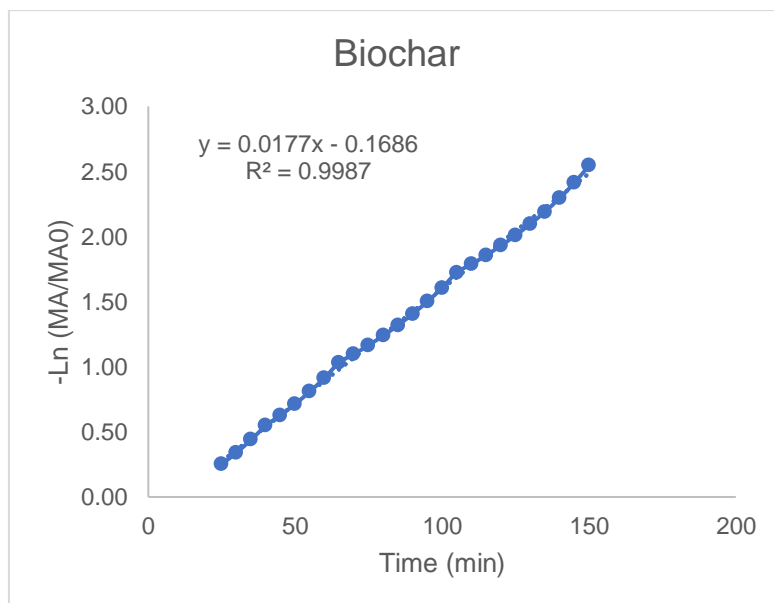


Figure A 7: Kinetic constant for catalytic cracking (Biochar)

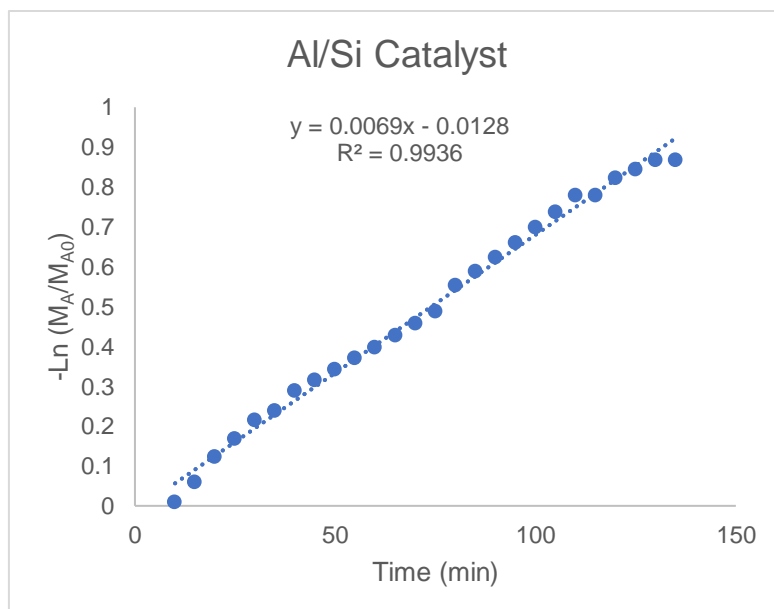


Figure A 8: Kinetic constant for catalytic cracking (Al/Si Catalyst)

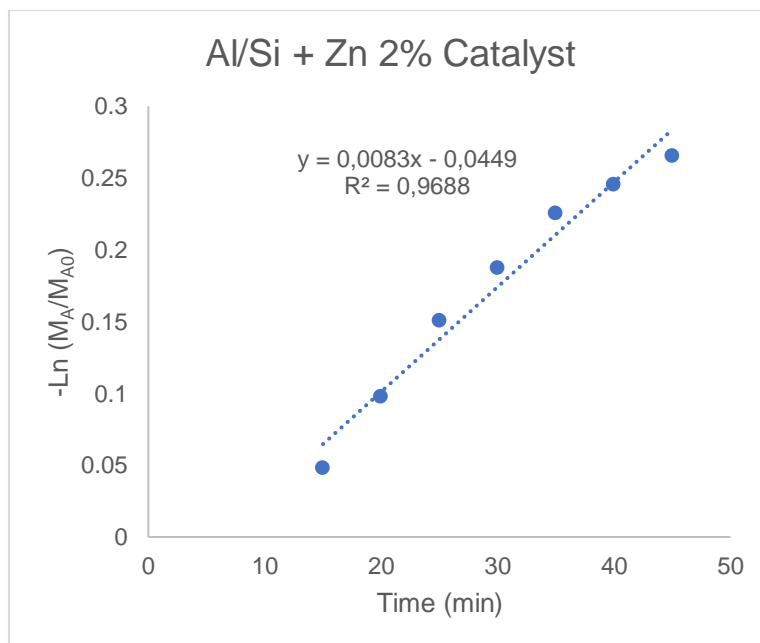


Figure A 9: Kinetic constant for catalytic cracking (Al/Si + Zn 2% Catalyst)

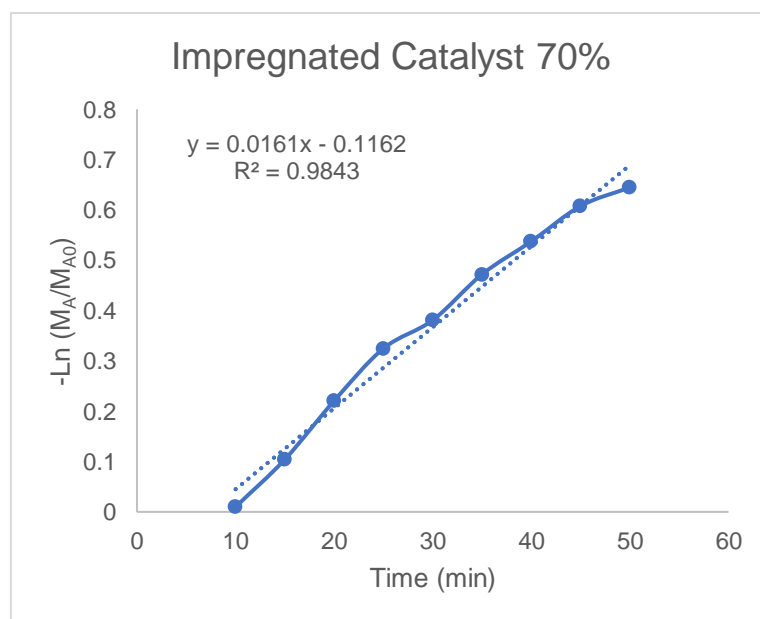


Figure A 10: Kinetic constant for catalytic cracking (Impregnated 70%)

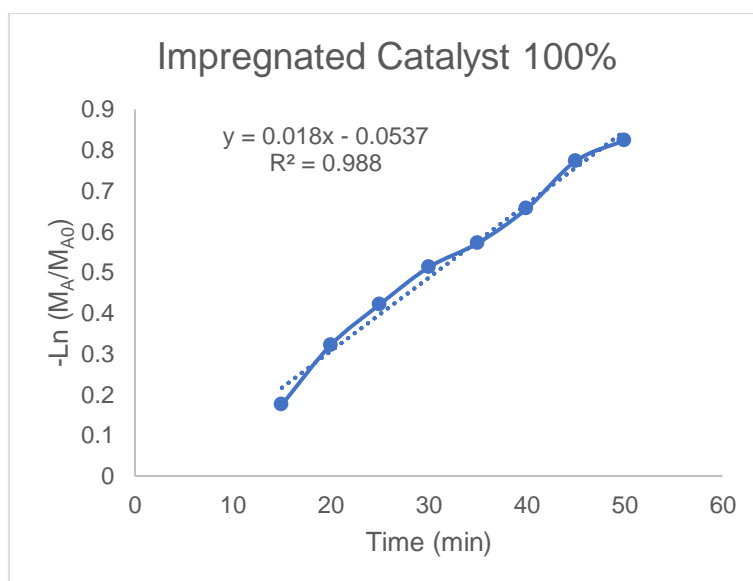


Figure A 11: Kinetic constant for catalytic cracking (Impregnated 100%)

Table A 1: Condensate Characterization

Relative Density	0.8761
Viscosity 40 °C	2.76 m ² s ⁻¹

