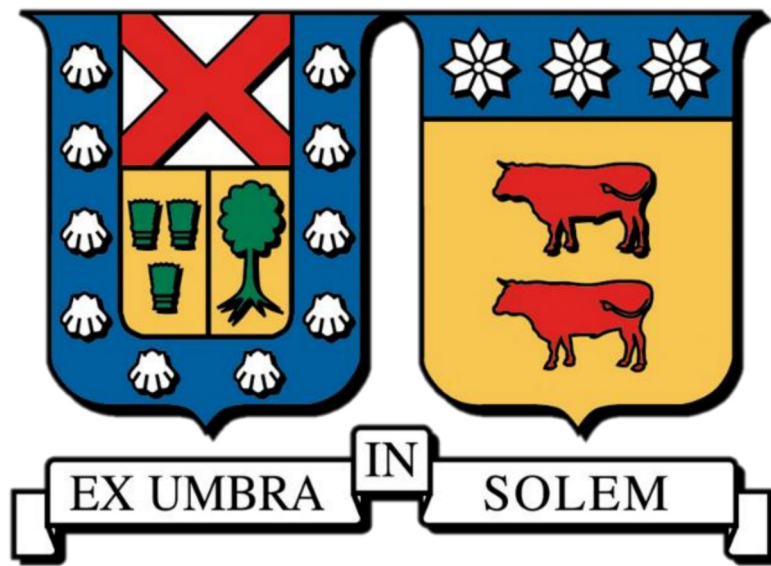


Universidad técnica Federico Santamaría



Methanol production from exhaust gases of siderite direct reduction with hydrogen

Technical evaluation for the catalyst characteristics and
optimal process conditions

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Engineering thesis

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Abstract

The mining industry worldwide is responsible for approximately 7% of the overall greenhouse gas emissions (GGE), reaching in Austria alone 15% of the national emissions. As a solution to this problem, there is a process that is capable of directly reducing the iron ores to elemental iron only with the use of H_2 eliminating the emission intensive steps such as roasting and furnace plants, unfortunately due to the intrinsic characteristics of the mineral iron, this process is only capable of eliminating 60% of the overall emissions, generating as a byproduct a gaseous stream rich in CO, CO_2 y C_xH_y . With the main objective of breaching the gap between the 60% reduction and a fully clean mining process, the revalorization of the stream on a reactor catalyzed by CuMgO, converting the carbon oxides into methanol in an effective, efficient, and sustainable way. To reach this goals, different process conditions were evaluated, varying the composition of the catalyst from 10% to 40% wt.% Cu, the calcination temperature of the MgO from 550°C to 1300°C, the reaction pressure within 30 to 50 bar and evaluating different recirculating loads within the system from 20 to 120 times over the feed gas. It was observed that the best results are obtained at 20wt.%Cu, with a calcination temperature of 1300°C, 50 bar of system pressure and a circulating load equal to 100 times over the feed, achieving values of 80% yield of conversion of the fed CO_2 to methanol.

Resumen

La industria minera alrededor del mundo es responsable por un 7% de las emisiones de GEI, alcanzando en Austria un 15% de las emisiones nacionales. Como solución a este problema, existe un proceso de reducción directa del mineral de hierro utilizando H_2 reemplazando una planta tradicional, desarrollado por TU Graz, sin embargo el proceso solamente logra reducir las emisiones en un 60% debido a que se genera CO, CO_2 y C_xH_y al eliminar las impurezas de la mena. Con el objetivo general de aproximarse lo más posible a un proceso libre de emisiones, se propone la revalorización de esta corriente rica en CO_2 , CO y H_2 en un reactor catalizado por CuMgO generando metanol, de manera eficiente, con un alto porcentaje de conversión y menor degradación posible del catalizador, para posteriormente realizar una aproximación hacia un sistema de escala industrial. Para lograr los objetivos se evalúan diferentes condiciones de operación, variando la composición de cobre en el catalizador entre 10 y 40%, la temperatura de calcinado para obtener el MgO entre 550-1300°C, la presión de operación entre 30-50 bar y variando la carga circulante del sistema 20-120 veces respecto a la alimentación para poder concluir respecto a las mejores condiciones de operación. Observándose que los mejores resultados se obtienen con un 20% de cobre en el catalizador, con una temperatura de calcinado de 1300°C, 50 bar como presión de operación y una carga circulante de 100 veces la alimentación, alcanzando valores de hasta 80% de eficiencia en conversión del CO_2 alimentado hacia metanol.

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Introduction

The current mining industry is responsible for immense amounts of carbon emissions and waste generation, to shift the regular iron mining processes into a cleaner process, the TU Graz developed a solid-gas tubular reactor where it has been proven the technical feasibility of the direct reduction of iron carbonates and oxides into pig iron using hydrogen as a reduction agent, resulting in an over 90% of metallization and a 60% reduction in the carbon emissions. Nevertheless, the composition of the mineral ores always contains carbon, resulting in the 40% that has not been eliminated by the direct reduction. To close the gap between the 60% and a 100% emission free mining, it is proposed to include an extra processing step consisting in the hydrogenation of the exhaust gases. Although some technologies for reducing carbon emissions have been used; such as carbon capture and underground storage, this step only represents energy consumption with no revalorization of the stream, the proposed catalytic reaction, utilizing a in-house built MgO/Cu catalyst is an end-of-life, clean solution to the presented problem, being able to valorize the exhaust stream into methanol, a widely bulk utilized chemical with efficiencies reaching up to 80% in the lab-scale experimentation phase, reflecting on a 90-95% of total emissions mitigation, when compared to the traditional mining process.

This report will be focused on the implementation of a revalorization catalytic carbon hydrogenation process, where the exhaust gases from the direct reduction can be used as a feedstock for methanol production. The objective of this work is the synthesis of a functional catalyst and evaluate the possible variations in the composition, calcination temperature of the support material and copper percentage, thus driving the conclusion about the best option for the desired reaction, as well another objective is to evaluate the different process configurations to obtain the most efficient process possible, varying different operating pressures, circulating load within the system, reaction times, and operating cycles, measuring the efficiency of the process both in overall yield of methanol produced, catalyst activity, reaction time and the real time composition of the gas mixture within the reactor.

Summary of contents

Section 1: The general background context for the experiment is presented, highlighting the importance of this report within the current contingency.

Section 2: The legal background for the chemical species involved in the process is presented to be taken into consideration.

Section 3: Theoretical background is provided to better understanding of the changes that would be involved within the mining industry to make the experimentation relevant in a real-life scenario.

Section 4: The experimental methodologies that are going to be used for the experimentation are listed, with the objective of depicting as objectively as possible how the experiment is conducted.

Section 5: The results of the experiments are presented, with all the parameters used and the calculations required, the objective is to present all the information obtained from the experimentation to later selection.

Section 6: Analysis and discussion of the results obtained in the previous section; the objective is to summarize the most important indicators in an easy-to-understand way, highlighting the best obtained scenario.

Section 7: Confection of a process design proposal using the results obtained in the previous sections, as well a monolithic tubular reactor is proposed for future studies based on previous works.

Section 8: A Simulation of the process on an industrial scale to assess an analysis of sensibility, and to general robustness of the idea.

Section 9: General conclusions and professional recommendation about the experiment and for future development.

1. General background and context

To have a clear view of the importance of CO₂ mitigation worldwide is presented in this section, highlighting some of the impacts that this investigation can lead to and the current global objectives regarding the carbon emissions reduction goals, the shift to lean production and the importance of energy carriers in the future.

1.1. World Outlook

In order to achieve the Net Zero Emissions (NZE) scenario provided by the World Energy Outlook (WEO) [1] and stabilize the global rise in temperature at 1.5°C by 2050, is imperative to adapt the whole energy, extraction and production industry towards an efficient and sustainable way of work; electrification of the industry and clean energy production are the main topics when it comes to sustainable development, but so as to make this happen, the mining industry plays a crucial role, providing the majority, if not all, of the key components that allow the existence of clean energy, the whole concept of electrification and clean energy production does not exist without iron, copper, heavy and rare metals, therefore it is impossible to achieve sustainability without starting with a change on the current mining and refining methods.

Worldwide, mining is responsible for approximately 7% of all carbon emissions[2], in Austria alone, mining represents 13% of the national footprint [3], this is mainly due to the conversion step required to get a purified material from the ore. Specifically in Austria, the iron ores are found in carbonate form (siderite), then is necessary a calcinating process to oxidize it, followed by a reduction with either coal or methane in a blast furnace, both being highly energy intensive processes with substantial CO₂ emissions reaching two tons CO₂ per ton of steel [4]. While the recycling technologies are becoming more popular each year, its only projected to reach 44% of the net steel worldwide demand [5], leaving the rest of it to the mining industry to fulfill. In this vein, is possible to replace this two-step process changing the reduction agent from coke to hydrogen, eliminating the calcination step, directly reducing the siderite to iron with a high carbon content, referred in the industry as pig iron, although this would not eliminate the emissions due to the carbonates in the mineral's composition that must be eliminated in some way, by changing the reduction agent the overall emissions are reduced by more than 60% [6], and the exhaust gas obtained by this process can be

repurposed in a catalytic reaction to produce methanol and methane, resulting in a clean, emission free mining process, without the need of non-renewable materials or fuels, producing a valuable non-fossil fuel with a high demand in the industry [7].

While the feasibility of the reaction has already been proven, the off-gas treatment to close the breach between the 60% emissions reduction and a clean production has not been yet considered, in it the results for methane production from the gases already have been satisfactory, reaching CO₂ yields of over 85%. [6], while the research on the methanol production is still not conclusive yet, with no existent literature regarding the comparison of multipurpose catalysts, achievable yields, or efficiencies nor optimal conditions for the reaction.

1.2. Chile as a potential leader in the hydrogen economy

To fully comprehend the hydrogen production potential of Chile or any place on earth, it is first necessary to establish what “green hydrogen” is, and its importance on the current global market.

Hydrogen is the first and most basic molecule on the universe, as well as the most abundant in it, yet currently 90% of the hydrogen produced in the world come from fossil fuel processes [8], which implies considerable amounts of carbon emissions, this is grey hydrogen, making the resulting hydrogen in most cases, even less ecological than commonly used fuels reaching over 110 gCO₂/MJ.[9] Nevertheless, processes like natural gas reforming (NGR) with carbon capture systems (CCS) or water electrolysis, present a clean, environmentally friendly solution for the hydrogen carbon footprint [10], if the energy used on this processes come from a renewable energy source (RES), here is where the country of Chile could play a crucial role in the future.

Due to the wide variety of ecosystems in Chile, such as the Atacama Desert, being the place on earth with the highest solar radiation [11], or the extreme austral climate on the southern-most sector of the country, one of the few places on earth where the wind power on-shore is the same as off-shore [12], and crossing through a wide variety of climates in between those extremes, making the country as the main place in the world regarding potential for green energy production, with more than 1800 GW estimated RES capacity [13], meaning 70 times the amount of electricity consumed by the whole country and thus making it a potential energy exporter.

Naturally, and opposed to fossil fuels, renewable energies cannot be directly exported nor stored, they need to be converted into what is known as an energy carrier, this being a physical way of storing such energy in a safe and efficient manner. One solution to this problem is water electrolysis, due to the natural abundance of water in the south of Chile and the increasing advances on desalinization technologies, hydrogen can be directly produced by any RES, converting direct current electricity produced by Eolic or photovoltaic sources into a fuel with a high gravimetric energy density such as hydrogen. Unfortunately, although hydrogen can be stored and transported, doing it implies high energy consumption in compression and expensive materials for the high-pressure tanks[14], or an even higher energy consumption for cryogenic liquid storage, therefore making convenient the idea of using the hydrogen as a precursor to a more dense, ideally liquid, energy carrier such as methanol, ammonia, or other tailored liquid organic hydrocarbons (LOHC) [15].

1.3. Methanol as precursor and energy carrier

Given the situation of hydrogen by itself not being the most optimal way of transporting and storing energy, multiple alternatives have been reviewed, ranging from solid matrix storage on iron for long overseas transport, gaseous storage in tanks doped with adsorbents, to liquified molecules that can release hydrogen or directly being used for energy or chemical purposes [15].

On this vein, methanol is a widely, bulk used, chemical with an annual worldwide consumption of 90 million tons [16] and is also frequently used as a gasoline additive to reduce the knock inside the pistons of the ICE [17] and increasing the overall combustion efficiency [18], but apart from that, its physical properties such as liquid form at atmospheric conditions and high stability [19], added its heat capacity, energy density and viscosity, makes it a viable replacement for traditional liquid fuels like petrol or gasoline without the need of any major changes on the current transport network or grid [20].

Traditionally methanol production relies on the syngas conversion to methanol, a process that uses fossil fuels as the main raw material, making it a non-carbon neutral component, shifting the precursor to methanol from syngas to CO₂ obtained from mining refining processes, not only will help mitigate the emissions of the mining industry but will also generate a low-carbon fuel compatible for use on traditional ICE.

2. Legal and regulatory background

In this section, an overlook on the legal background and international regulations is taken regarding the two main chemicals involved in the process such as hydrogen as a reactive and methanol as the product, both highly inflammable and explosive, require precautions to manage, store, transport, and work with it.

2.1. Hydrogen legal regulations

Hydrogen technologies and development although being around since beginning of the 20st century, have gained accelerated interest around the globe, due to different fossil fuels crisis, the massification of batteries and electrical systems as a replacement for traditional ICE technologies and the combined effort across the world to decrease carbon emissions, forcing the governments of the world to start regulating and controlling the normative for the production and usage of hydrogen.

Depending on the country and the purpose of the use of hydrogen, there is a wide variety of normative regulating the production, conditioning, storage, transport, environment, and use of hydrogen either as a fuel, energy carrier or reactive. For this report, the international regulations from are reported since most of the countries and industries use this as the main parameter to determine the operation.

Table 1 International hydrogen normative[21]

Sector	Int. Regulation	Detail
Hydrogen production	NFPA 2 / 13	Hydrogen generation systems
	ISO 16110	Hydrogen generators using fuel processing technologies
	ISO 22734	Hydrogen generators using electrolysis technologies
Conditioning	ANSI/CSA HGV 4.8	Hydrogen fueling station compression guidelines
Storage	NFPA 2 / 7	Gaseous hydrogen storage
	NFPA 2 / 8	Liquified Hydrogen storage
	ASME (BPVC)	Boiler and pressure vessel code
	CGA H-2	Classification and labeling of hydrogen storage systems with metal hydride adsorbents
	EIGA 100 / 11	Hydrogen cylinders and transport vessels

	ISO 16111	Transportable gas storage devices
	UE 2010 / 35	Transportable pressurized equipment
Transport	ASME B31.12	Hydrogen piping and pipelines
	EIGA 121/14 (CGA G5.6)	Hydrogen pipeline systems
	EIGA 15/06	Gaseous hydrogen stations
	EIGA 06/19	Safety in storage handling and distribution of liquid hydrogen
	CE 2008 / 68	On-road hazardous materials transportations
	49 C.F.R. 171-180	Hazardous material regulations

As of Chile, the regulations regarding this area, are still on an incipient stage, nevertheless since 2020 and widely approved by the parliament of the country [22], a national future policies and strategy plan for the development, regulation, and incentives regarding green hydrogen with projections to the year 2050. Due to the strong growth that renewable energies have had and the projected growth on the upcoming years, Chile has been a focus specially for the European and Asian energetic market, incentivizing the effort on updating the existent and create new regulations to improve the national development of hydrogen technologies.[11]

2.2. Methanol legal and health regulations

The main objective of this work is to evaluate the technical feasibility of the methanol production from an exhaust gas feed, thus is necessary to take into consideration the factors that determine the quality of the produced methanol and the regulations regarding this chemical. Since methanol is a widely used reactant, there is an extensive regulatory framework both nationally and internationally. For this report's purposes, it is going to be considered an international one, since is often, as well as hydrogen, that most of the regulations are based on this ones.

According to the methanol institute, methanol is an organic, hygroscopic, noncolored, fully water miscible liquid alcohol, classified as a volatile solvent and a light density fuel (0.8 g/cm^3). Under certain circumstances, methanol vapor within storage tanks is considered an explosive, also on liquid form it retains its flammability even at high water

concentrations.[23] Methanol is also classified as a toxic substance, which can be absorbed in the skin and small amounts can produce permanent blindness, while over 30 mL can result in death [24].

Table 2 Shows a summary of the international regulatory framework regarding the Health and safety on the workplace, environmental, transportation, disposal, and shipping regulations.

Table 2 International Methanol regulations [25]

Sector	Int. Regulation	Detail
Occupational Safety and Health	29 CFR 1904	Recordkeeping
	29 CFR 1910.20	Access to exposure and medical records
	29 CFR 1910.119-120	Process safety on hazardous waste and materials
	29 CFR 1910.132-139	Personal protective equipment
	29 CFR 1910.146-147	Confined space
	29 CFR 1910.151	Medical aid
	29 CFR 1910.1000	Air contaminants
	29 CFR 1910.1200	Hazard communication
Environmental	40 CFR 61	Emission standards for hazardous air pollutants
	40 CFR 68	Accidental gas releases
	40 CFR 141	Safe drinking water
	40 CFR 260-269	Waste management
	40 CFR 302-355	Release of hazardous substances planification and notification
Transport	49 CFR 107	Hazardous material program procedures
	49 CFR 171-180	Carriage by rail, vessel, highway. Specification for tank cars, packaging, and maintenance.
	49 CFR 191	Gas pipeline safety procedures
	49 CFR 195	Hazardous Liquids transportation by pipeline

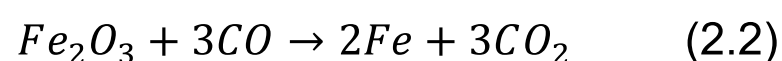
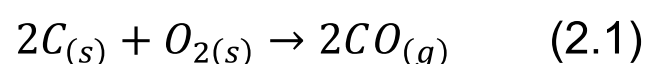
Navigation and Water	33 CFR 126	Explosive handling within or contiguous waterfront facilities
	33 CFR 130	Financial responsibility for water pollution
	33 CFR 153-167	Control, transfer, prevention and safety for oil and hazardous materials
Shipping	46 CFR 2	Vessel classification
	46 CFR 151	Bulk liquid hazardous material cargoes.

3. Theoretical background

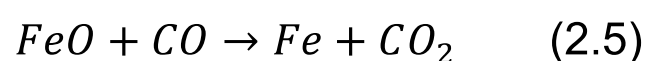
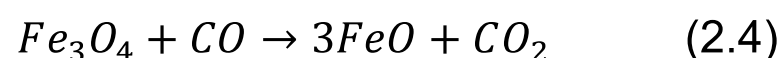
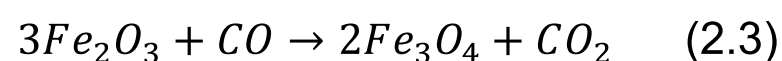
In the following section the theory behind the experiment is analyzed, going over the necessary topics such as how the iron mining industry works nowadays, how the direct reduction could replace it and how could the catalyzed hydrogenation help close the gap to achieve a “lean mining”, putting in context the importance and the role of the carbon hydrogenation and the impact of shifting the traditional blast furnace mining into a reaction mining, especially when it is done with a process that reduces the emissions even further such as the proposed.

3.1. Iron producing

The process of obtaining iron from any ore consists of the elimination of unwanted species contained in the mineral, this species may vary from a wide range of components, and it depends on the characteristics of the environment, the ground, the depth of the mineral vein, the presence of water, other minerals, among much other variables [26]. In the case of iron, it is commonly found in the form of magnetite, hematite, goethite, limonite and siderite, siderite being the only carbonate of the group while the others are oxidized minerals. The oxidized ores are directly reduced by the combustion of mineral carbon (coke) in a blast furnace, a unit operation shown in figure 1, where the mineral is mixed with coke and limestone, to later be reduced by the rapid, countercurrent combustion of the coke, using the CO to eliminate the oxygen in form of CO₂.



While the overall reaction does not show extensive amounts of carbon emissions, there is several intermediate reactions that heavily affect the net CO₂ generation only in the reduction process [27].



As well, the usage of limestone for the removal of impurities, silica, also generates carbon emissions [27].

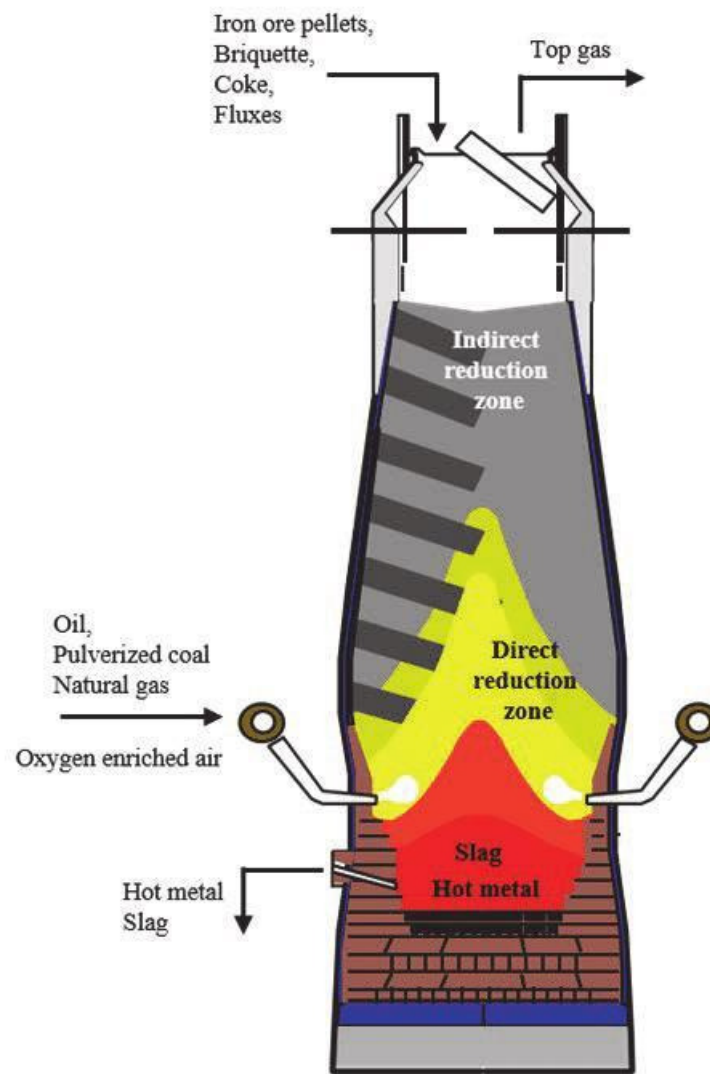
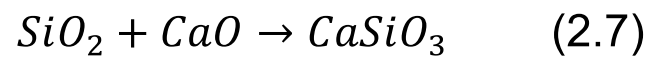
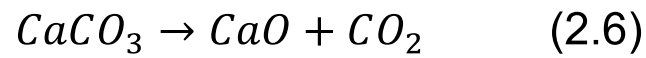
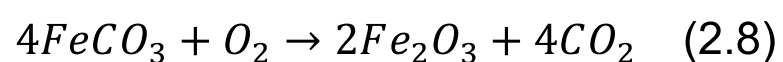


Figure 1 Diagram of a traditional blast furnace

On the other hand, siderite is the only iron carbonate bulk-used to produce pig iron, and due to this specific characteristic, it makes the mineral especially hard to directly reduce it in a blast furnace or any type of reverb furnace, thus the process requires an extra calcination step [6]. The calcination step consists, usually of a vertical cylindrical reactor (calciner oven) on which the carbonate ores are heated up with limited amount of air, driving the thermal decomposition of the carbonates as seen in equation (2.8), naturally this extra step in the process requires fuel and energy to heat up the system, resulting in more carbon emissions due to the energy consumption and the intrinsic carbon that must be removed in form of carbon oxides.



3.1.1. TU Graz process of Siderite direct reduction

The process of oxidizing from iron carbonate to oxide, and then reducing it to pig iron, can be replaced by only one direct reduction step, on which hydrogen acts as the sole reduction agent, going directly from the carbonate to the elemental form of iron, as observed on Figure 2 and Figure 3, in order to achieve the metallization of the iron ore, either being oxide or carbonates, the utilized hydrogen must be in a considerable excess, making also the process to require mildly high temperatures ranging from 500 to 800 °C is considerable less energy intensive as the average temperature of a blast furnace is over 1500 °C as well as the reverberatory furnace, and directly cutting off the calcination step. To make this process possible, a sealed fix bed reactor shown in Figure 4 is required, since hydrogen is highly explosive in presence of oxygen and thus air, as well as the powdered iron produced, it can easily and quickly re-oxidize, in a highly exothermic reaction creating a hazardous operation, therefore, the atmosphere of the reactor must be thoroughly controlled, as well, the entire system needs an efficient and effective neutralization and extraction system. The flow into the reactor is manually controlled by the operator online with a PLC system connected to volumetric flow controllers as well as the pressure of the system by a pneumatic pressure valved located in the exhaust of the reactor, allowing the operation of a gas analyzer and a micro gas chromatograph (MGC) both of which can only operate at atmospheric pressure. The whole reactor is located inside an extraction bell system to collect the ventilation gases and any gas filtration that may exist.

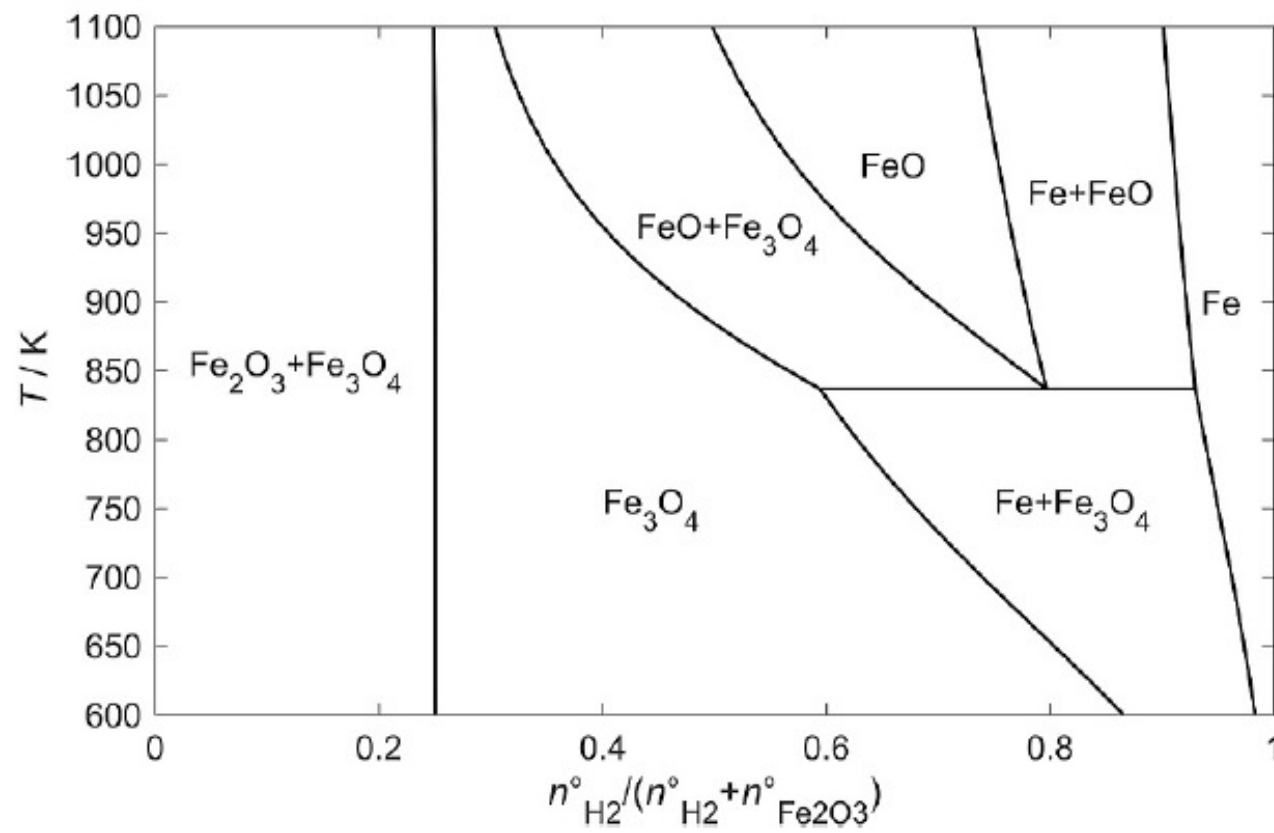


Figure 2 Equilibrium solid phase diagram of a Fe₂O₃-H₂ system [28]

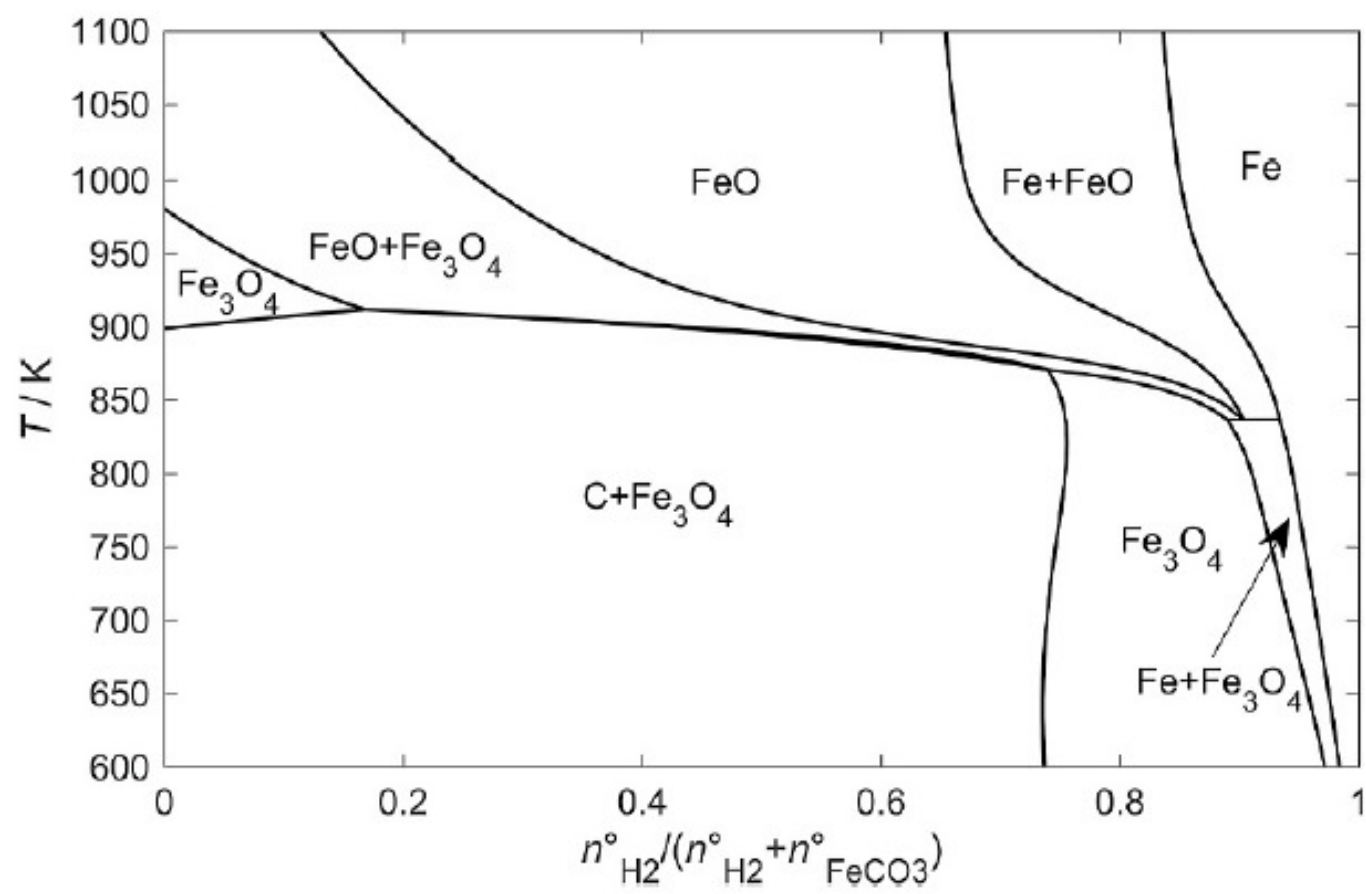


Figure 3 Equilibrium and solid phase diagram of a FeCO₃-H₂ system [28]

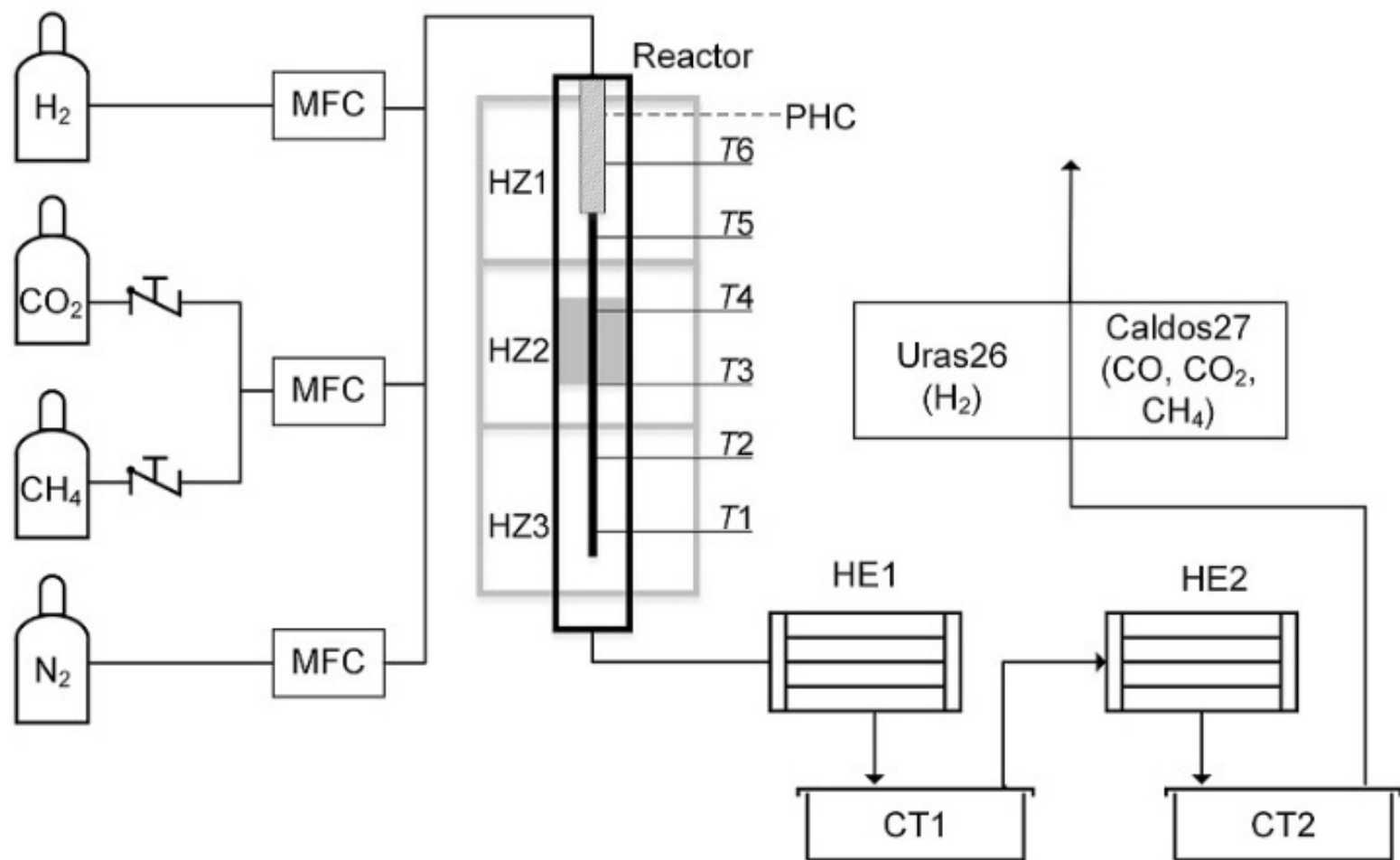


Figure 4 Fixed-bed reactor setup with mineral iron carbonate sample fixed[29]

Although being less energy intensive and generating less carbon emissions, the process of direct reduction with hydrogen is not free of CO_x emissions, since the ore has carbon in its structure, it's inevitable to eliminate it without generating some form of carbon oxides, resulting in an exhaust gas composed mainly by excess unreacted hydrogen, CO_2 and CO from the reduction, water, and methane, an exhaust gas with this composition, is considered syngas this being a mixture of elements that can be used as the feedstock for the synthesis of wide range of valuable products, such as methane, methanol, ammonia, naphtha, toluene, ethylene glycol, among other more specific compounds.

3.2. Methanol production

Methanol is a transparent, flammable, and toxic component and the shortest carbon chain alcohol liquid at ambient conditions, is used in the chemical industry as the precursor to a variety of hydrocarbons, olefins, acetic acid, formaldehyde as well as an additive to gasoline in order to improve the octane number making the combustion of it more energy efficient [30], lately it has also been considered as a potential energy carrier as it has a considerable higher energy density compared to hydrogen, easily biodegradable and the possibility producing it using green hydrogen for its production means that is an option for a green, low emission and carbon neutral fuel.

For the methanol production, the process is based on a series of catalytic reactions that to the date, their mechanism of functioning is not completely known [31], nevertheless the most widely accepted theory describes it as an interface reaction where the H_2 is adsorbed in the surface of the copper part of the catalyst and then is split into H^+ , while the carbon components (CO , CO_2 , or methane) are adsorbed in the promoter, this component of the catalyst being MgO , ZnO , NiO , TiO , or a mixture of them [32], once this happens, the reaction occurs in the interface between the copper surface and the promoter, forming after the chain reaction is complete, the desired methanol that can be easily separated from the product stream due to its boiling point of $65^\circ C$, at atmospheric pressure. For similar reasons as the reduction reactor, in this case the reaction must take place in an airtight reactor, on which the catalyst is fixed, and where the feed stream is pumped into, recirculating it while the liquified methanol is retained in the bottom of the condenser. The diagram of the constructed reactor for the experimentation is shown in Figure 5.

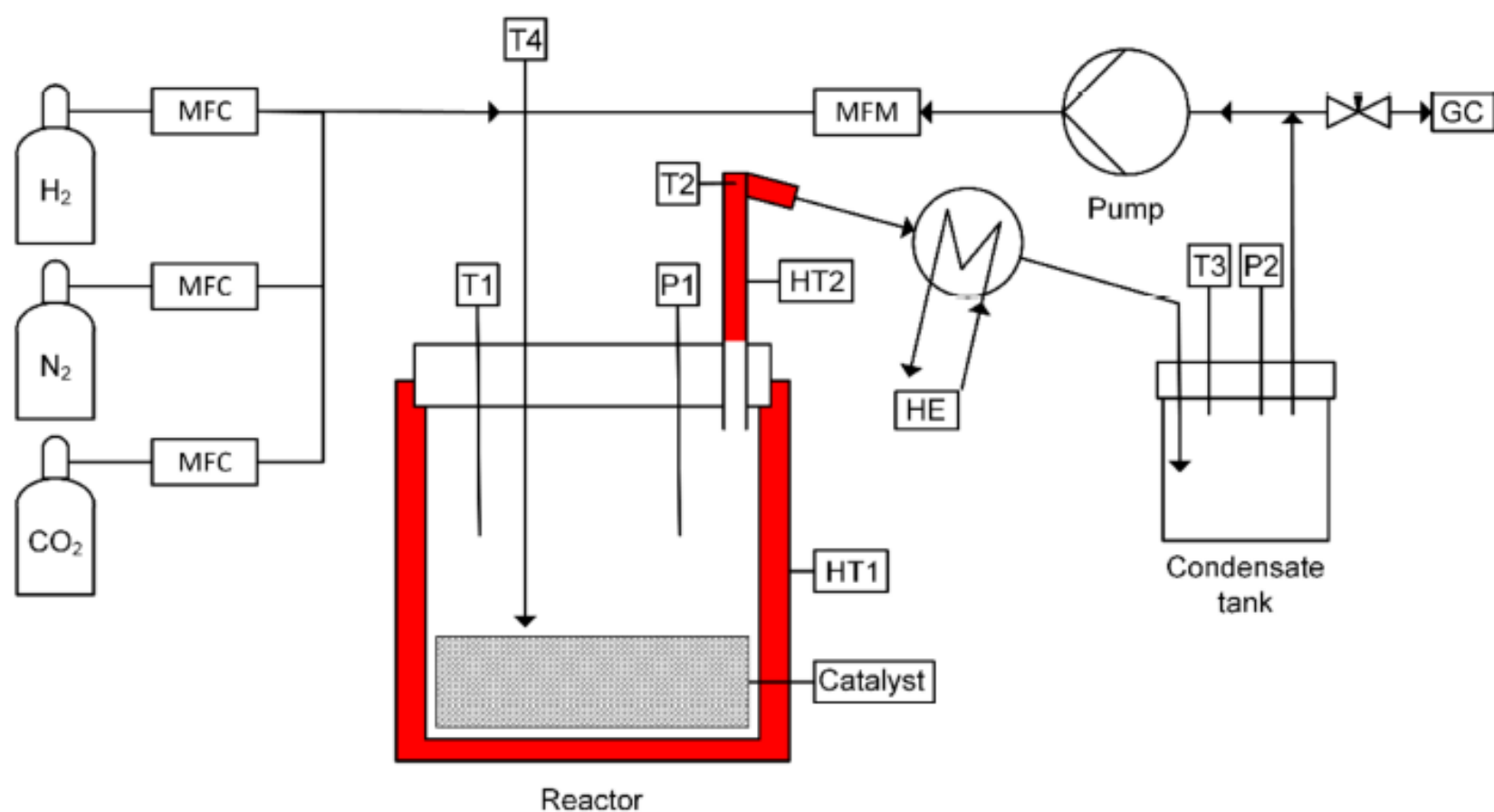


Figure 5 Experimental setup of the semi-continuous tank reactor with external recycle for the gaseous reactant stream and external condensation of condensable products [33]

Unfortunately, the reaction in the case of methanol, and opposite of methane is not thermodynamically favorable, as shown in Figure 6, resulting in a less efficient process and a poor conversion from carbon oxides to methanol, thus the catalyst configuration and composition must be tailored to maximize the aspects that allow the reaction to occur, them being copper dispersion, interface area between the promoter and the promoter and active surface/volume ratio.

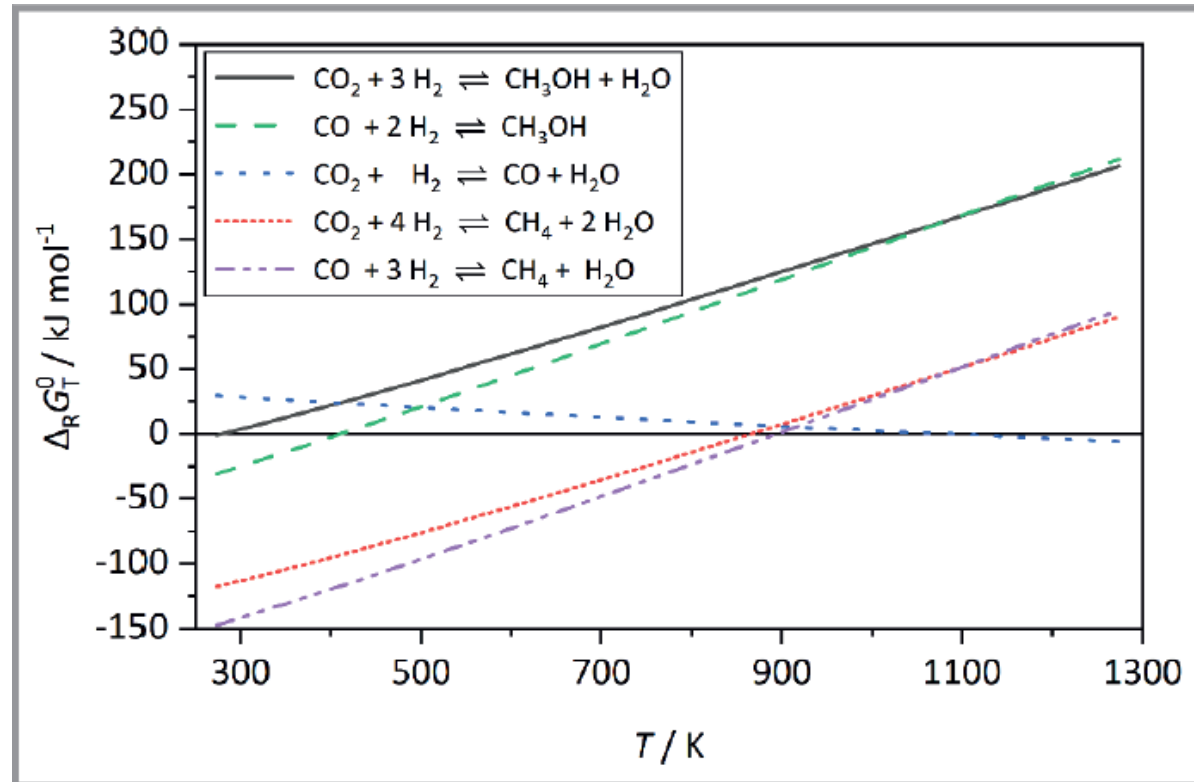


Figure 6 Standard Gibbs free energies of reaction for the RWGS reaction and the hydrogenation of CO and CO₂ to methane and methanol [34]

Overall, within the catalyst components there must be three main needs to be satisfied, one of the components makes the hydrogen splitting, in virtually every case, this is done in the copper part of the catalyst, then a promoter in where the carbon oxides are deposited and then hydrogenates, in the current commercial processes in the industry this role is done by ZnO, and lastly a supporter is needed in order to provide, structural stability and keep the copper and the promoter in small particle sizes, being Al₂O₃ the most common supporter. While in the methanol producing industry this catalyst characteristics are sufficient to get a satisfactory process, is not possible to replicate it due to the different composition of the feedstocks, commonly the syngas utilized in a regular methanol production facility comes from the gasification of coal, resulting in a mixture rich on hydrogen and CO, with small amounts of CO₂ and traces of methane, on the other hand from the iron direct reduction, the mixture is rich in hydrogen but the amount of CO and CO₂ is fairly equal, resulting in a rapid acidification of the promoter in the catalyst, poisoning it, consequently in order to reach a satisfactory conversion of carbon oxides to methanol, an improved catalyst configuration must be found.

4. Experimental methodologies

This section specifies the experimental steps, plans and methodologies for the experiments that will be performed, materials used, the reactor specifications and providers, software and instruments utilized as well as the variables that are going to be used as a measure of the results in the experiments.

4.1. Catalyst composition

The catalyst used for the methanol production, must count with two main components; a copper active area and a base support of MgO, this last component with the specific objective of making possible the recycling of the spent catalyst through the steel purification process once the catalyst is worn off, since MgO is widely used as a slag former in the steel industry [35]. Unfortunately, the MgO supporter has an unsatisfactory effect when used alongside copper with no promoter fulfilling the role of capturing the carbon oxides and allowing the interface reaction [32], mainly due to the MgO behaving both as a supporter and promoter simultaneously, but not doing a good enough work in any of it [31], consequently the addition of a purposed promoter is needed in the catalyst, allowing the MgO act solely as the support or the promoter, so the overall yield is improved and therefore the feasibility of the process is achieved.

In order to find the ideal promoter, it's first necessary to found the optimal composition of Cu-MgO, to the date there is no research so far about the different catalyst activity when the Cu/MgO ratio is changed, this information is crucial for the purpose of obtaining both a technically and economically feasible project, for if a high enough efficiency is reached only varying this aspect of the catalyst, is arguable that is more convenient to use a less efficient catalyst over developing a new, more complicated one that also add complexity to the recyclability of the project.

In the case that a satisfactory efficiency is not reached with only Cu and MgO, the best iteration of the experimentation can be upgraded by the addition of a promoter, since the reaction of hydrogenation of carbon oxides is yet to be fully understood [32], in the literature there is plenty of discussion regarding which supporter, promoter and in what ratio they should be used [36], nevertheless some of them can be selected based on the amount of investigation around them that has already been done, the economic

availability of the component and the possibility of recycling it when it's already been used. for this case, the chosen promoters are ZnO and TiO₂.

4.1.1. Cu-MgO catalyst synthesis

The first objective of this research is to find the optimal configuration of the base Cu-MgO catalyst, which is synthesized by a wet impregnation method with copper nitrate trihydrate and MagGran®, for its preparation the following steps are followed.

- (1) Preparation of MgO: Calcination of MagGran® in a muffle furnace for 5 h in air at 723 K followed by 2 h at 823 K.
- (2) Wet Impregnation: The calcined MgO is impregnated with the copper nitrate solution, cooled in a stirred flask for 2 h to later be filtered and dried overnight.
- (3) Thermal decomposition: The catalyst is calcinated for 1 h at 432K followed by 5 h at 723 K.
- (4) Activation of the catalyst: The CuO-MgO is reduced in a semi continuous tank reactor with a feed gas mixture of hydrogen and nitrogen for 3.5 h at the CO₂ hydrogenation reaction condition.

This process must be repeated varying the ratio between the copper and the magnesium, to conclude the optimal composition for later use of such composition in the promoter's experimentation.

4.1.2. Cu-MgO-ZnO (CZM) catalyst synthesis

As previously mentioned, for a satisfactory yield of carbon conversion, the action of three components is needed: a hydrogenation copper active area, a supporter, and a promoter. The first candidate as a promoter to be evaluated is zinc oxide, the combined effect of the zinc and magnesium oxides has shown a favorable synergy in conditions with high CO₂ and CO combined [36].

For the preparation of CMZ, the next steps are followed, according to Zander et al. [37]:

- (1) 75 [g] of 1.0 M of Cu/Mg (7:3) is co-precipitated at 338 K with a precipitating agent of 1.6 M Na₂CO₃ to form hydroxycarbonates in a stirred tank reactor at a pH of nine.

- (2) The precipitated is aged for 2 h in the mother liquor to later filtration and dried. The obtained crystals are impregnated with 4.0 [mL] of 0.27 zinc nitrate solution.
- (3) The resultant mixture is calcinated in static air for 3 h at 623 K.

4.1.3. Cu-TiO₂-MgO (CTM) catalyst synthesis

Another promising option for a synergic effect on the Cu-MgO based catalyst is the addition of titanium dioxide, for this case, the proposed roles are switched, with the TiO₂ acting as the supporter of the system and the MgO as the promoter, implying that the proportion of the catalyst is mostly TiO₂. Following the studies of Guo & Mao Et al. (ref), the use of titanium dioxide with the addition of 1wt% magnesium oxide improves drastically the conversion of CO₂-rich streams as well as the copper active specific area. [38]

For the CTM preparation, a wet impregnation process with a hydrothermal method, following the next steps.

- (1) The preparation of the TiO₂ supporter, first 2.0 [g] of hexamethylene tetramine is added to a 45.7 [mL] of methanol and 50 [mL] of distilled water solvent, to later add 4.3 [mL] of titanium trichloride 15wt% dropwise into the solution.
- (2) The resulting solution is put into a 200 [mL] autoclave for a hydrothermal treatment at 363 K for 1 h followed by a 463 K for 2 h.
- (3) The resulting mixture contains white titanium dioxide crystals, which must be vacuum filtrated and washed with ethanol until no chlorine is detected. The resulting powder is dried overnight at 353 K.
- (4) The addition of MgO is done by wet impregnation with Magnesium nitrate, using the amount corresponding to 1wt% of the obtained titanium oxide on step (3), Then, the resulting product is dried overnight at 383 K and then calcinated at 673 K in still air for 4 h.
- (5) Lastly, the copper is added by the impregnation of the MT precursor with copper nitrate reaching a loading of ideally 10wt% of the supporter media. The impregnated samples must be dried overnight at 383 K and then calcinated at 673 K for 4 h.

4.2. Direct reduction reactor

The operative conditions of the direct reduction system utilized, presented on Figure 7 are; a feed stream composed of 90% H₂ and 10% N₂ with a flow of $0,05 \left[\frac{m^3}{h} \right]$ where nitrogen is utilized purely as a trace element for mass balances purposes, as both equipment for gas sampling, ABB Uras26 and ABBCaldos27 both multi gas analyzing systems, report the results in volumetric percentages, thus knowing the amount of nitrogen, an inert compound, can be used to calculate the real mass value of the rest of the components.

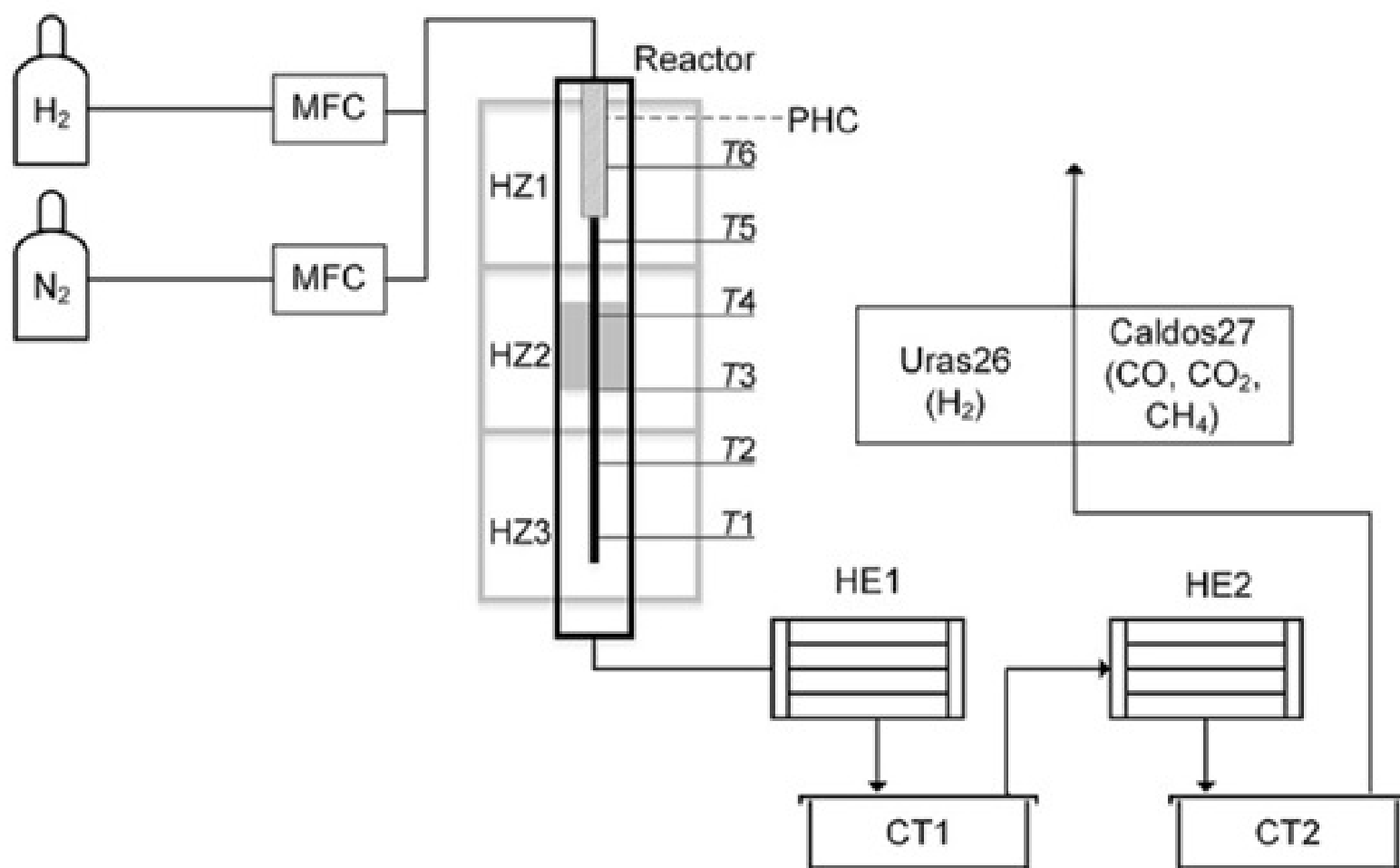


Figure 7 Direct Reduction utilized system.

4.2.1. Reactor configuration

The direct reduction reaction is executed on a tubular reactor provided by Parr Instruments, used as a packed bed on which 100 [g] crushed iron ore is placed. Hydrogen is injected into the tubular reactor at different pressures depending on the experiment, varying between atmospheric pressure up to 70 [bar], nevertheless, this is only for research-data retrieving only, since a pressurized hydrogen-iron process is hardly feasible on a real-life industrial scenario. The gas injected to the system does only one pass through the reactor, thus making it an open system, the startup of the reaction is

carried out until the gas analyzer placed on the bottom of the reactor detects 90% hydrogen, while the remaining 10% is nitrogen also being injected into the system, to make possible the mass balance since the gas analyzer only reports the volume percentages of the exhaust gas.

Once the desired hydrogen concentration is reached, the heating jacket of the reactor is activated, to increase the temperature of the system up to 700 °C, for the past experiments have shown that this temperature is the optimal for the direct reduction of the siderite ore (Figure 8)[39].

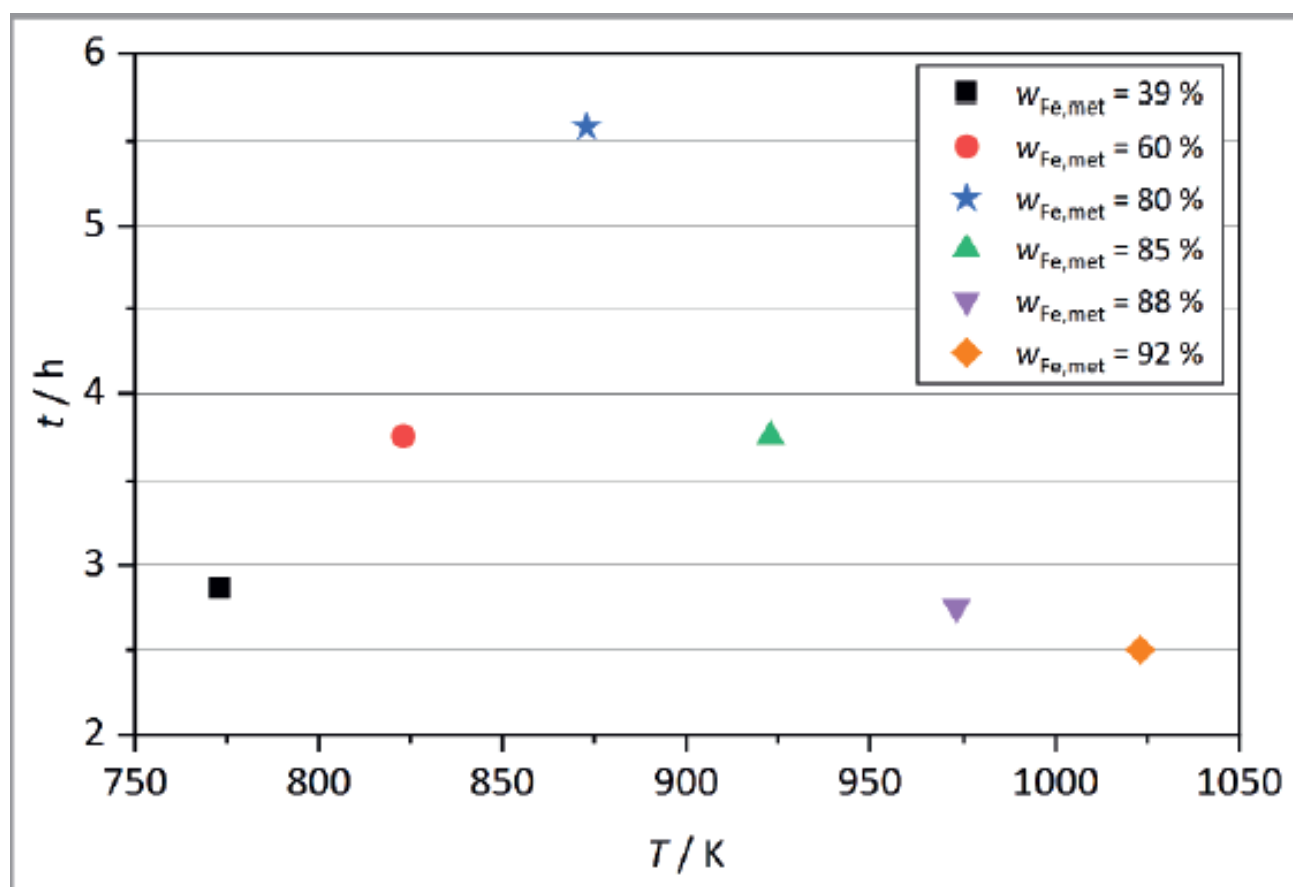


Figure 8 Effect of the reduction temperature on the reduction time, each point is reported as the reached degree of metallization[39]

During the heating up of the system, the reaction of reduction will start, showing concentrations of carbon oxides and methane in the gas analyzer, nevertheless, the reaction will continue until the 90% of hydrogen is reached once again indicating that there are no more products being formed and consequently only detecting the inlet gases. During the reaction, the concentration of carbon oxides reached at this process conditions (Figure 9) is approximately 20% CO₂ and 10 % CO, the rest being mainly unreacted hydrogen and traces of methane[39].

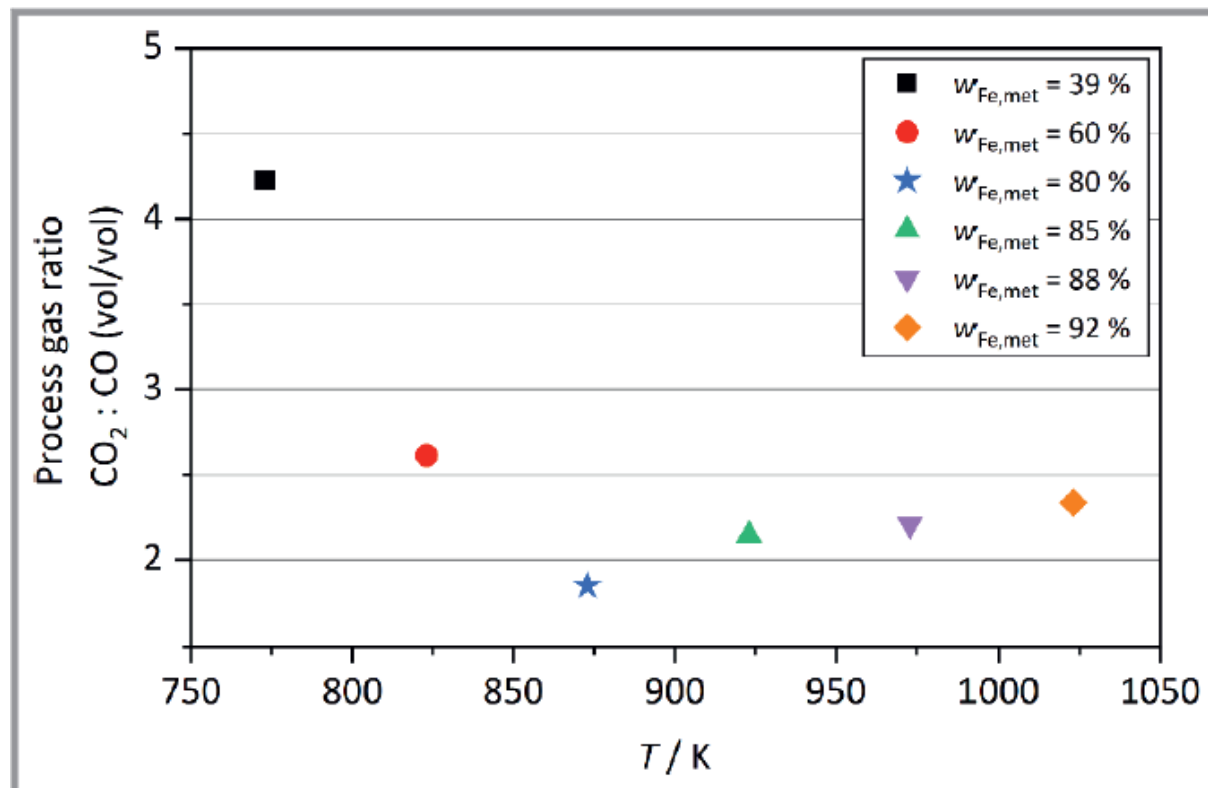


Figure 9 Temperature effect over the dioxide: monoxide ratio on the exhaust gases from the direct reduction [39]

The experimentation is done with different iron ores, provided by the VA Erzberg mining company, located in Erzberg, 70 km to the northwest of Graz. The provided iron ores vary from a wide variety of minerals from the traditional siderite extracted from the Erzberg mine to different imported ores to use as comparison such as magnetite from IOC or hematite from Carajas, Brazil, Finland, among others.

For the extraction of the product, since is powdered pig iron, is susceptible to a quick and highly exothermic oxidization, then is necessary to take it out with a constant flow of nitrogen, and immediately store it on a sealed flask, preventing the oxidation to cause mistakes on the calculations.

4.3. CO₂ Hydrogenation reactor

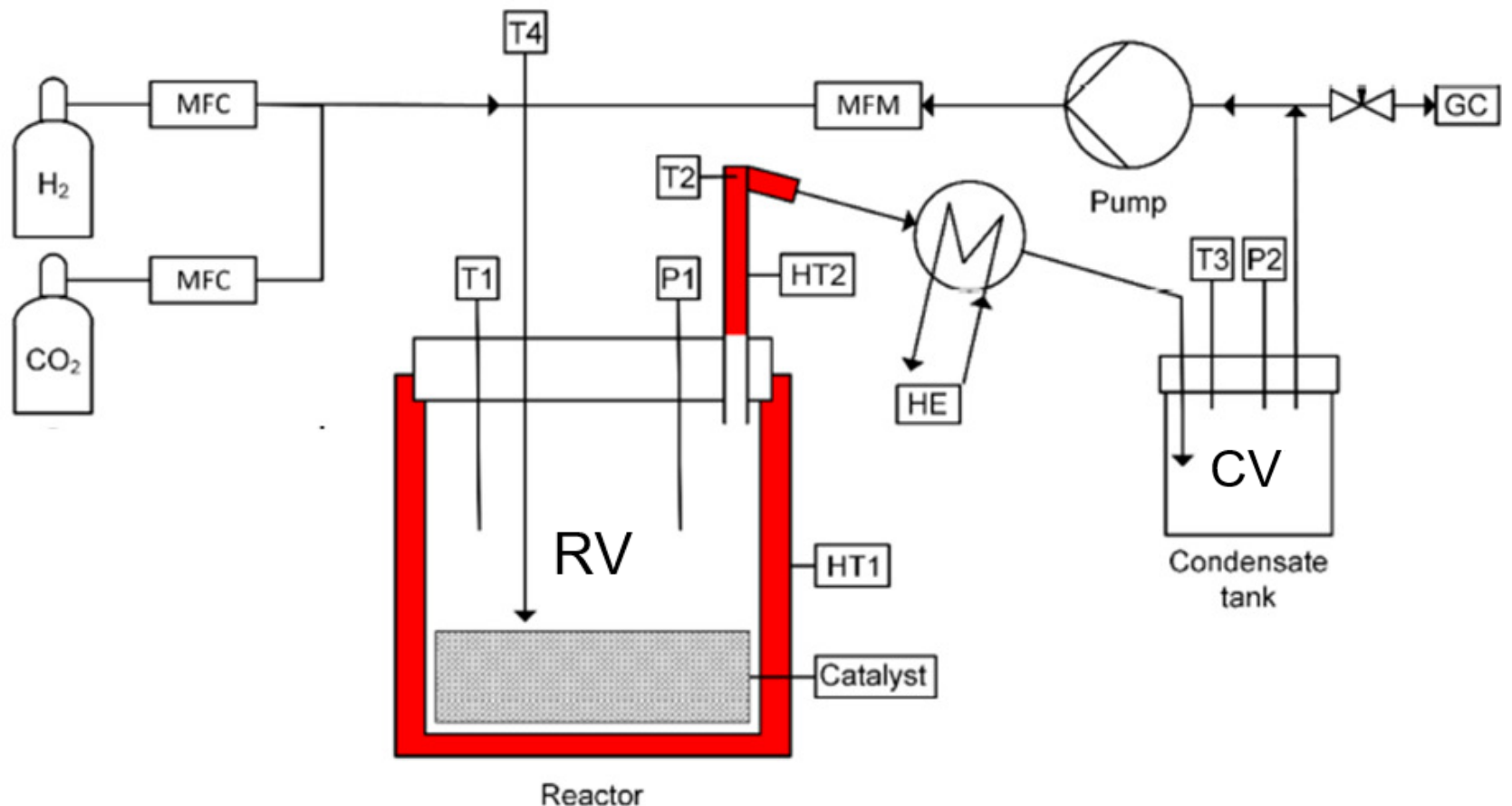


Figure 10 Utilized reactor for the experimental setup.

4.3.1. Reactor configuration

The catalytic carbon hydrogenation reaction shown in Figure 10, is executed a semi-continuous recirculating system consisting in a main reactor vessel (RV) where 8 [g] of powdered catalyst is placed and the feed gas is injected generating what is believed to be a fluidized bed-like effect, naturally forcing the solid-gas interaction, a condensation vessel (CV) on which the product is collected in liquid form, thus extracting it from the system and pushing the reaction equilibrium towards the products, while the remaining gases are recirculated by a peristaltic gas pump at different flowrates in the range of 0,5 to 6 NL/min, into the RV again. The feedstock comes from a pressurized bottle that contains 25% CO₂ and 75% hydrogen, since the reaction is a volume-negative reaction and one of the products is extracted from the system, the bottle is left open at the operation desired pressure, constantly compensating for the volume loss while the reaction is executed as well as the gas loss due to the micro-GC (GC) samplings.

4.3.2. Reactor operation procedure

The operation of the reaction consists in a series of steps to make sure that the experiment can be done in a safety and correct manner:

- (1) Pressure testing: since the reaction is conducted at a mildly high pressure of 50 [bar] with presence of explosive and highly flammable reactants, it is necessary to evaluate the tightness of the system, starting with nitrogen. The nitrogen is pumped into the system in 10 [bar] steps, on each of them checking all the valves and fittings with leak fluid, to detect any leaking that might exist. Once the test with nitrogen is completed, the system is depressurized and then the same procedure is repeated with hydrogen, checking again every fitting and valve but using instead a hydrogen sensor, to detect minor leaking that might exist.
- (2) Catalyst activation: when the system is already airtight and depressurized, the next step is the activation of the catalyst, for this, the powdered catalyst is placed inside the RV with a funnel, then the system is filled with hydrogen with a mass-flow controller at a rate of 400 [Nml/min] to prevent flushing away the catalyst from the RV. When the system reaches 35 [bar] the pump is activated at a flowrate of 0,6 [L/min], followed by the activation of the heating system. After the temperature reaches 300 °C, the pressure inside the system must be adjusted to 50 [bar] as well as the flowrate of the pump to 1 [L/min]. The system is left in these conditions for 3 hours to later cool and depressurize.
- (3) Main Reaction: to start the reaction, the feedstock bottle is changed to fill the system with the CO₂-H₂ gas mixture, the system is flushed for 15 minutes using a mass-flow controller at a rate of 500 [Nml/min], once the system is flushed, the pressure must be incremented to 35 [bar], to later start the heating and recirculation of the system. When the system reaches 300 °C, the pump must be configured to a flow of at least 1 [NL/min] not exceeding 6 [NL/min] the bottle is left opened to make up for the volume loss. The micro-GC and the mass-flow sample controller is set to take duplicate samples every hour after two and a half minutes of flushing, allowing the visualization of the progress of the reaction.

4.4. Experimental variables and indicators

Since the hydrogenation of CO₂ is a reaction which has not been fully understood, and thus the reaction mechanisms are partially unknown, the main objective of the experiments is to do a thermodynamical and kinetic analysis of the reaction, to find the conditions on which the conversion to CO₂ is both stable and efficient. For this, there are two main aspects to consider, the first and most important one, the yield of methanol produced over the amount of CO₂ that was fed to the system, the yield of the reaction is going to be calculated as proposed in equation 4.4.1:

$$\gamma_{MeOH} = \frac{MeOH[mol]}{CO_2[mol]} * 100\% \quad (4.4.1)$$

Yet, the yield is based on the amount of gas input during the reaction, and it does not consider the efficiency of the overall process, then to make it possible to compare this effect across all the experiments, the variable efficiency is defined as equation 4.4.2:

$$\eta_{MeOH} \left[\frac{gMeOH}{h} \right] = \frac{M_{product}[g] \cdot X_{MeOH}[wt. \%]}{t[h]} \quad (4.4.2)$$

The second aspect to consider of the suitability of the tested catalyst is the time it requires to achieve the reaction equilibrium. At this point, the system is on a constant reactive gas concentration, meaning that the system is resistant to changes in the feed without affecting the methanol production, making it a relevant point for a potential scale up of the process. The equilibrium point is identified using the CO concentration variation on time defined on equation 4.4.3:

$$Plateau = \frac{dCO}{dt} \left[\frac{\% mol}{min} \right] = \frac{(CO_{t_i} - CO_{t_{i-1}})}{t_i - t_{i-1}} = 0 \quad (4.4.3)$$

Then the stabilization time is given by the moment when the equilibrium point is reached.

4.4.1. Catalyst copper loading experiments

The first batch of experiments are meant to observe the best catalyst composition for Cu/MgO impregnated catalyst, to achieve this 4 experiments are going to be conducted at 50 bar, 300°C and 80 hours of reaction time, varying the catalyst between 10wt.%,

20 wt.%, 30 wt.%, and 40wt.%, all of them prepared by wet impregnation method described on 4.1.1.

Due to the long duration of the experiment, and the fact that a new catalyst is needed for every one of them, it is performed on a weekly basis, consisting of; one day of disassembly, cleaning and later pressure test of the reactor, the next day the catalyst is placed inside the reactor and the activation is performed, finally the reaction is started ideally on a Friday, so the 80 hours consist of Friday, Saturday, Sunday and the morning of Monday, fitting exactly one full experiment cycle each week.

Once the reaction is over, the reactor is depressurized and cooled down, the product vessel is disassembled and the liquid product is taken out, weighted and the density is analyzed on a gas chromatograph, to calculate the amount of methanol produced during the experiment.

As previously mentioned, the best performing catalyst is going to be used for the following experiments.

4.4.2. Pump flow rate experiments

The system counts with a peristaltic gas pump that fulfills the purpose of moving the gas from the reaction vessel to the product vessel, thus determining the residence time of the gases in the reactor, and since the reaction is strongly thermodynamically unfavorable, the extraction of product gases will have a significant effect on the overall yield of the reaction, nevertheless, the amount of flow input by the pump can, if it's not handled carefully, flush the catalyst from the reactor to the product vessel, both stopping the reaction and ruining the produced methanol.

To analyze the effect of pump flow, and thus the gas residence time, six shorter and consecutive experiments will be performed, without changing the catalyst from one experiment to another, each experiment has a duration of 24 hours, at 50 bar and 300°C, varying the pump flow from 0.5 [NL/min], 2 [NL/min], 4 [NL/min], 6 [NL/min], and then twice again with 0.5 [NL/min] to test the condition of the catalyst and the reproducibility of the performed experiment.

The catalyst is only activated once and before the first experiment, between each experiment the catalyst is flushed with nitrogen before the temperature decreases below 100°C to prevent water from the reactor atmosphere to condense over the catalyst,

and the methanol from the product vessel is taken out, weighted, and analyzed on the gas chromatograph to obtain the density and conclude the efficiency of each experiment.

Once the results of this experiment cycle are analyzed the best configuration is going to be used for the following experiments regarding catalyst degradation.

4.4.3. Catalyst degradation experiments

One of the most important characteristics of a catalyst is its degradation time and consequently, how reusable it is, the ideal scenario being no or very little degradation of the catalyst, since the principal goal of this investigation is the production of methanol, the capacity of the catalyst is going to be measured solely by the methanol yield, nevertheless, the concentration of CO over time is also going to be analyzed to observe if there is changes in the reaction mechanisms due to the reuse of the catalyst.

The experiments will be performed using one catalyst, and repeating the same experiment, aiming to make all the parameters as similar as possible with each other, unfortunately, the characteristics of the gas pump, makes the task of stabilizing the value of the flow without oscillations, to compensate this issue, the selected flow must be high enough, so the oscillations are less significant over the average flow. The experiment conditions are 45 bar and 300°C.

The catalyst is only activated once before the first experiment, after every reaction the system is flushed with nitrogen to prevent condensation and the liquid from the product vessel is taken out, weighted, and analyzed on the gas chromatograph.

4.5. Software and instruments utilized.

Since the reaction is performed in the mentioned semi-continuous tank reactor BüchiGlasUster Limbo350 with a rated volume of 450 [ml] at non ideal gas conditions, them being high pressure, and a reactive gas mixture, two mass flowmeters Bronkhorst EL-FLOW (MFM) and one mass flow controller (MFC) measure the input. MFM2 is positioned at the inlet pipe of the system, measuring only what is going into the system from the gas bottle, MFM1 is located after the recirculation pipe, measuring the mass of gas that is going into the reactor, and is used to monitor the pump flow, lastly the MFC1 is programmed to automatically open every hour to let a sample to be measured

by the MGC. All the mentioned instrument's measurements are logged into the software LabView as normal milliliters per minute ([Nml/min])

The progress of the reaction is monitored using an Agilent/Inficon microGC 3000 gas chromatograph, taking samples every hour, and reporting the mole fraction of the sample, nevertheless, the yield and efficiency of the reaction is only obtained once the reaction is over and the liquid product is extracted, since the MGC only reports what is observable in the atmosphere of the reactor, and it is hardly representative of how much methanol is being produced. The methanol is later analyzed by gas chromatography on a Shimadzu GC2010+ equipped with a flame ionization detector and Zebron ZB WAX+ column.

The recycling is performed by a Fink Ziclón 04 gas circulation pump, rated at 60 [NL/min] at standard conditions and 50 Hz but used at 25 Hz and a variable flow adjusted with recirculation valves to fit the experiment needs.

The gases are provided in a crystal mixture by AirLiquide, both the hydrogen and the Hydrogen- CO₂ mixture.

5. Experimental obtained results

In this section the results from the experiments realized are reported, to later be analyzed in Result analysis and discussion, the calculations to get to the reported values are explained and all the measurements are reported.

5.1. Methanol conversion from CO₂

As mentioned on the section 6, the methanol conversion experiments were done on a sequential order, to make sure that only one variable is analyzed at the same time and collecting the best results of each series of experiments and utilizing them as the starting point for the next ones.

5.1.1. Optimal copper loading

To determine the optimal copper loading on a Cu/MgO catalyst for methanol production, 4 experiments were planned to be executed, obtaining the results on Table 3.

Table 3 Copper loading obtained experimental data.

Experiment	Category	Catalyst	Hours	Avg reflux	Actual pressure	Product Vol	MeOH	wt.% MeOH	Yield	Efficiency
			[h]	[ml/min]	[bar]	[ml]	[g]	[%]	[%]	[gMeOH/h]
10wt.% CuMgO 1000ml/min Cu Load	Copper loading	10wt.% Cu/MgO 550°C	76.5	935.71	50.01	52.4	47.41	45.73%	56.42%	0.28
20wt.% CuMgO 1000ml/min Cu Load	Copper loading	20wt.% Cu/MgO 550°C	76.83	1068.14	49.27	74.67	67.8	50.52%	70.12%	0.45
30wt.% CuMgO 1000ml/min Cu Load	Copper loading	30wt.% Cu/MgO 550°C	76.47	1006.07	49.73	75.14	68.23	46.80%	66.02%	0.42
40wt.% CuMgO 1000ml/min Cu Load	Copper loading	40wt.% Cu/MgO 550°C	76.67	836.361	49.69	32.3	30.17	32.14%	37.96%	0.13

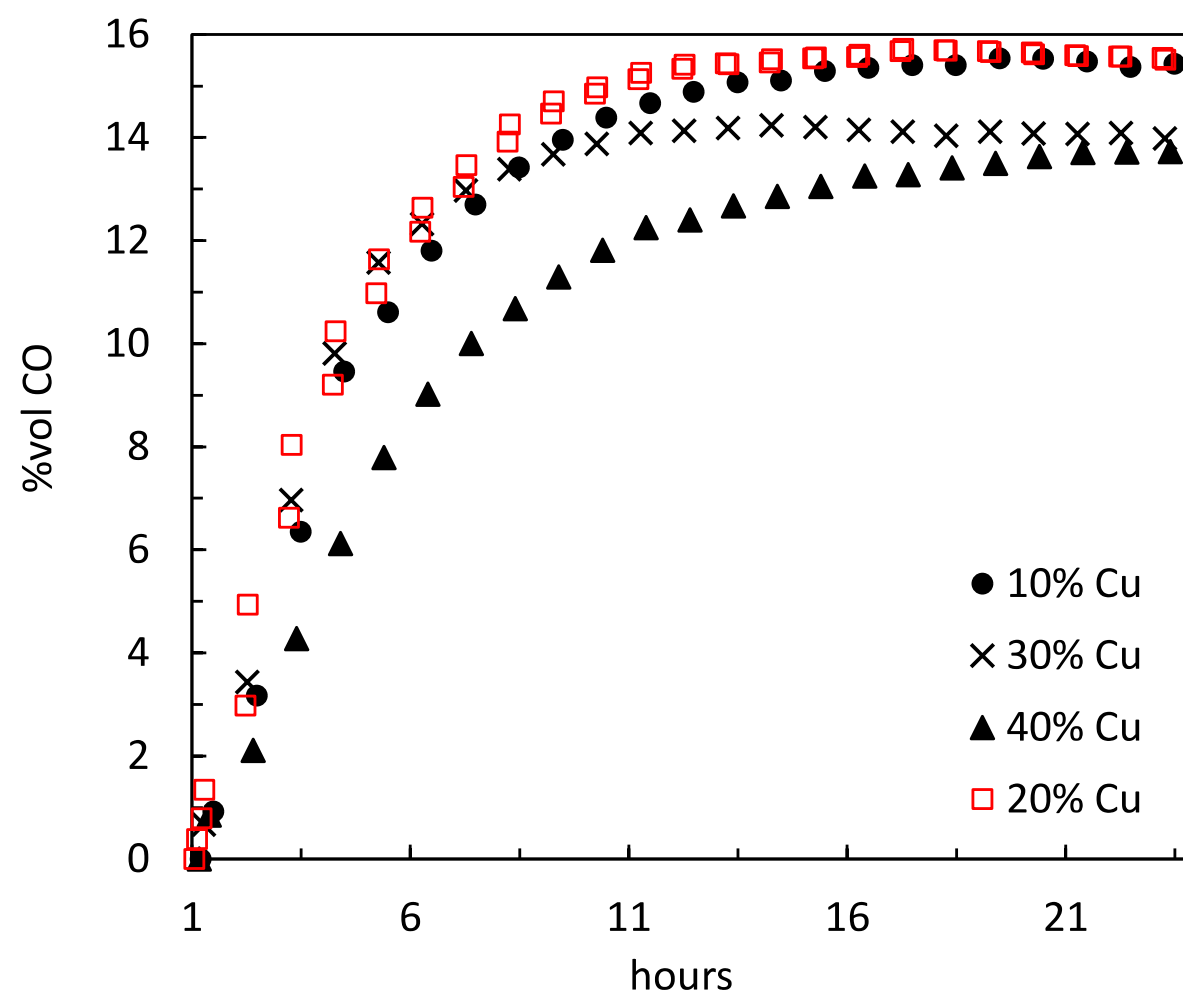


Figure 11 CO progression through the first 24 hours of experiment

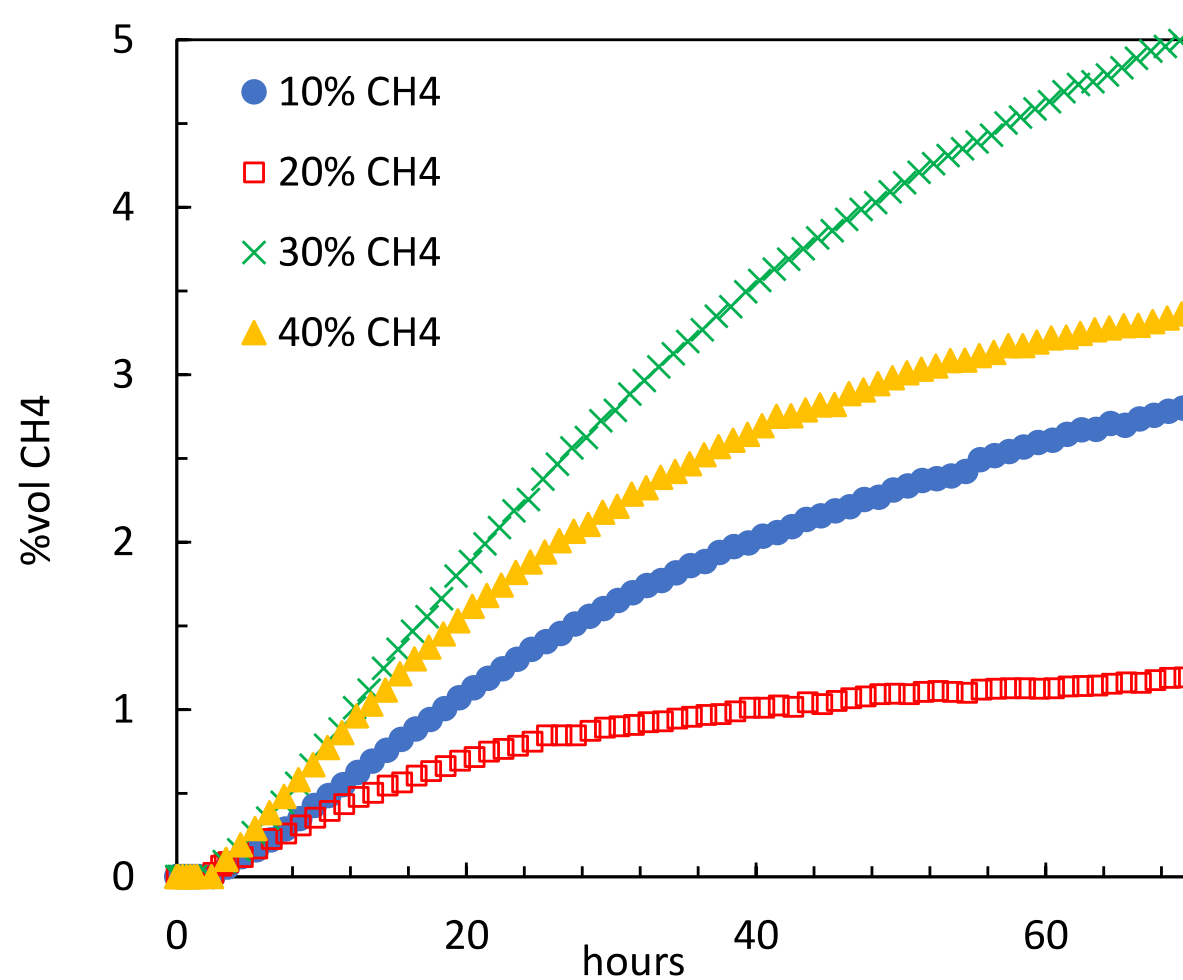


Figure 12 Methane progression through the experiment

To obtain the data presented on Table 3, it is necessary to do an integration of the report given by the MFC software mentioned on 4.5, since the software only gives the values measured by the mass flowmeters, pressure, and temperature. But for the estimation of the yield, it is necessary to have the mass of reactive input into the reactor

and the mass of product, the mass of reactive is estimated as presented in the equation (5.2)

$$V [Nml] = \int_{t=i}^{t=f} F_{CO} dt \quad (5.1)$$

$$V [Nml] = \frac{(F_{CO_{i-1}} + F_{CO_i})}{2} \cdot (t_{i-1} - t_i) \quad (5.2)$$

Nevertheless, the equation (5.2) represents a numeric integration, but the program logs all the inflow and outflow from the system, including the pressurizing, depressurizing and the samplings, flows that should not be considered since although they are happening during the experiments, they do not represent mass that is being used to generate any product. Since the pressure at the beginning of the experiment is the same that in the end of it, it can be assumed that the inflow from the initial time to the pressurization time is the same amount of outflow when depressurizing the system, thus considering $t = i$ as the time when the heating starts, and $t = f$ as the time when the reaction is stopped, before depressurizing.

Then, to subtract the amount of gas that is taken out of the system due to sampling, the activation of the MFC1 as a “flag” for detecting when the system is sampling, obtaining the sampling volume as described on equation (5.3)

$$\text{IF: } MFC1_i = !0, \text{ then Sample [Nml]} = \frac{(F_{CO_{i-1}} + F_{CO_i})}{2} \cdot (t_{i-1} - t_i), \text{ else} = 0 \quad (5.3)$$

$$V_{Rx} [Nml] = V - S \quad (5.4)$$

Finally, since the data is presented as normal milliliters, the mass of reactive is obtained as:

$$M_{Reactive} [g] = \frac{V_{Rx}[ml] \cdot 1[bar] \cdot 0.001 \left[\frac{L}{ml} \right] \cdot x_{reactive}}{0.0821 \left[\frac{L \cdot bar}{mol \cdot K} \right] \cdot 273.15[K]} \quad (5.5)$$

With the mole fraction of the reactive being a known factor obtained by the bottle's provider

Analyzing the data from the Table 3, the first conclusion that can be made is that the optimal copper loading for the Cu/MgO catalyst is 20wt.% followed by the 30wt.% when the analyzed factor is the yield of methanol produced, this meaning the efficiency of conversion from CO₂ to methanol, nevertheless, if the factor analyzed is the total amount of methanol produced on an hourly basis, both the 20wt.% and the 30wt.%

present very satisfactory efficiency, although the 20wt.% being better in both parameters, the two catalyst are going to be analyzed on the pump flow rate of the experiment, to compare if the superiority of the 20wt.% is just punctual or if it's a general characteristic of the catalyst. It is expected that the efficiency and the yield in the catalyst follow the same trend in any case, since the copper loading is a factor that affects the reaction of the synthesis, while the pump flow rate and the residence time is just a kinetic parameter being always limited by the rate of hydrogenation.

If the Figure 11 and Figure 12 are analyzed it is possible to notice that, contrary to the initial hypothesis, a higher concentration of CO achieved doesn't represent a better methanol yield nor a better efficiency, this being an unexpected result, due to the hydrogenation of CO being considerably more thermodynamically favorable than the direct CO₂ hydrogenation to methanol neither represent a bigger methane formation, due to the considerably higher concentration achieved on the 30wt.% experiment, being possible to conclude that, there is no direct correlation between the plateau of CO and the efficiency of the process.

It is important to consider the fact that the 30wt.% catalyst generates practically double the amount of methane than the 20wt.%, the obtained liquid will contain a bigger energy density due to the slight solubility of methane on methanol, making it an interesting consideration point if the objective of the product is to be a fuel, on the other hand, if the objective is to obtain the purest methanol solution as possible, without considering the water, this is easily separated by a flash separator thanks to the substantial difference on the boiling points of both compounds.

5.1.2. Pump flow rate (30wt.% Cu/MgO)

To determine the effect of the pump flow rate and the residence time of the gases on the reactor over the methanol yield and production 6 experiments were conducted, all of them with a duration of 24 hours, to analyze the difference on the gas composition along the experiments, the capacity of stabilize in short periods of time, and naturally the overall methanol production. The first 4 experiments were conducted changing the pump flow rate and the 2 last ones went back again at the first pump flow rate to prove the reproducibility of the experiment, the results are shown on Table 4, Figure 13 and Figure 14:

Table 4 Pump flow rate obtained experimental data.

Experiment	Catalyst	Hours	Avg reflux	Actual pressure	Product Vol	MeOH	wt.% MeOH	Yield	Efficiency
		[h]	[ml/min]	[bar]	[ml]	[g]	[%]	[%]	[gMeOH/h]
30wt.% 500 ml/min Flow rate	30wt.% Cu/MgO 550°C	24.37	523.6	49.26	19.60	18.03	0.437	59.30%	0.32
30wt.% 2000 ml/min Flow rate	30wt.% Cu/MgO 550°C	24.23	1841.6	48.98	28.81	26.22	0.474	67.46%	0.51
30wt.% 4000 ml/min Flow rate	30wt.% Cu/MgO 550°C	24.30	3877.9	50.647	38.77	35.44	0.497	73.35%	0.73
30wt.% 6000 ml/min Flow rate	30wt.% Cu/MgO 550°C	24.38	6273.9	50.55	44.39	40.13	0.5	74.45%	0.82
30wt.% 500 ml/min Flow rate 1st rep	30wt.% Cu/MgO 550°C	24.25	518.7	50.64	20.20	18.46	0.479	62.43%	0.36
30wt.% 500 ml/min Flow rate 2nd rep	30wt.% Cu/MgO 550°C	24.28	559.6	50.56	19.91	18.24	0.463	60.95%	0.35

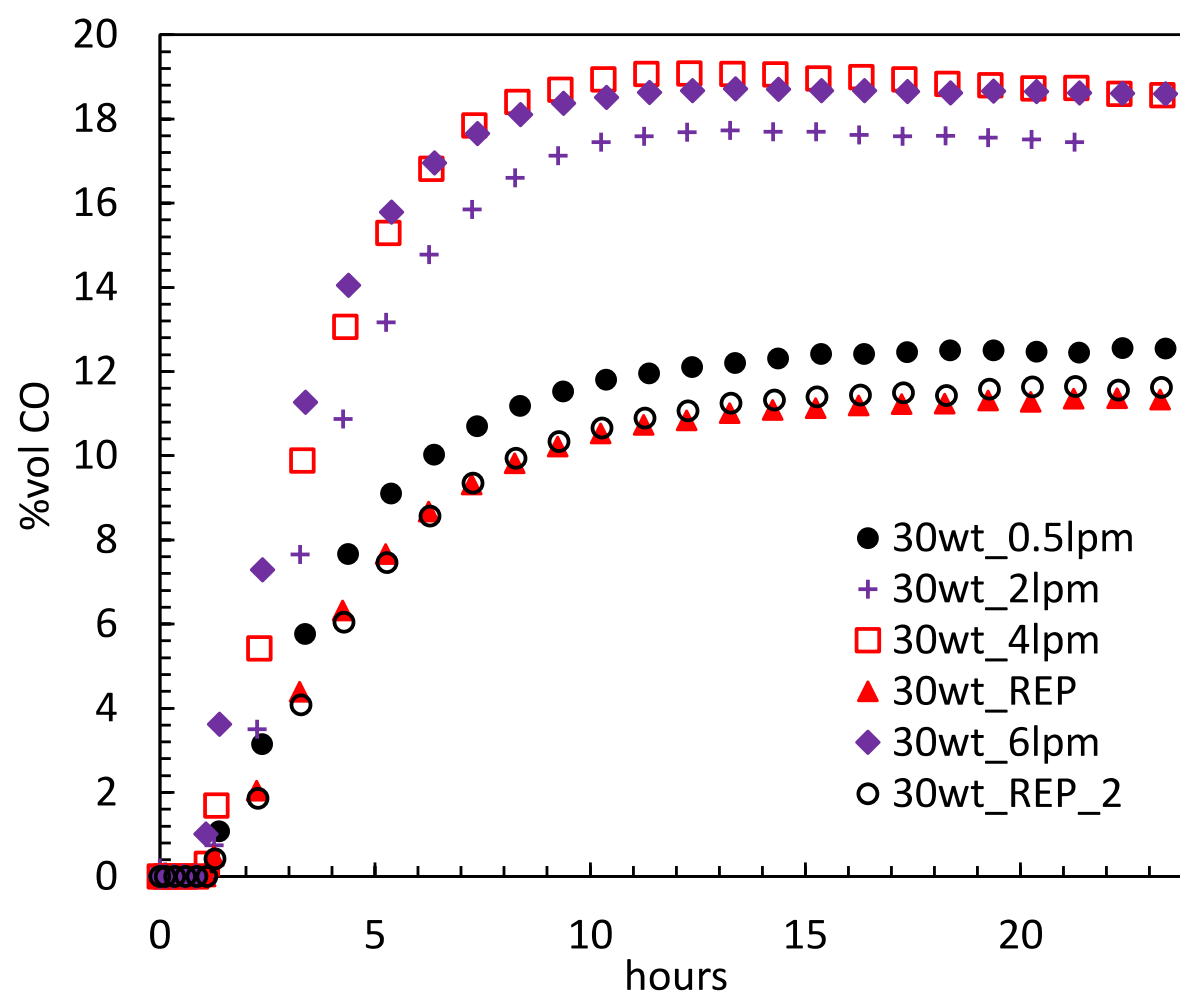


Figure 13 CO progression through the first 24 hours of experiment

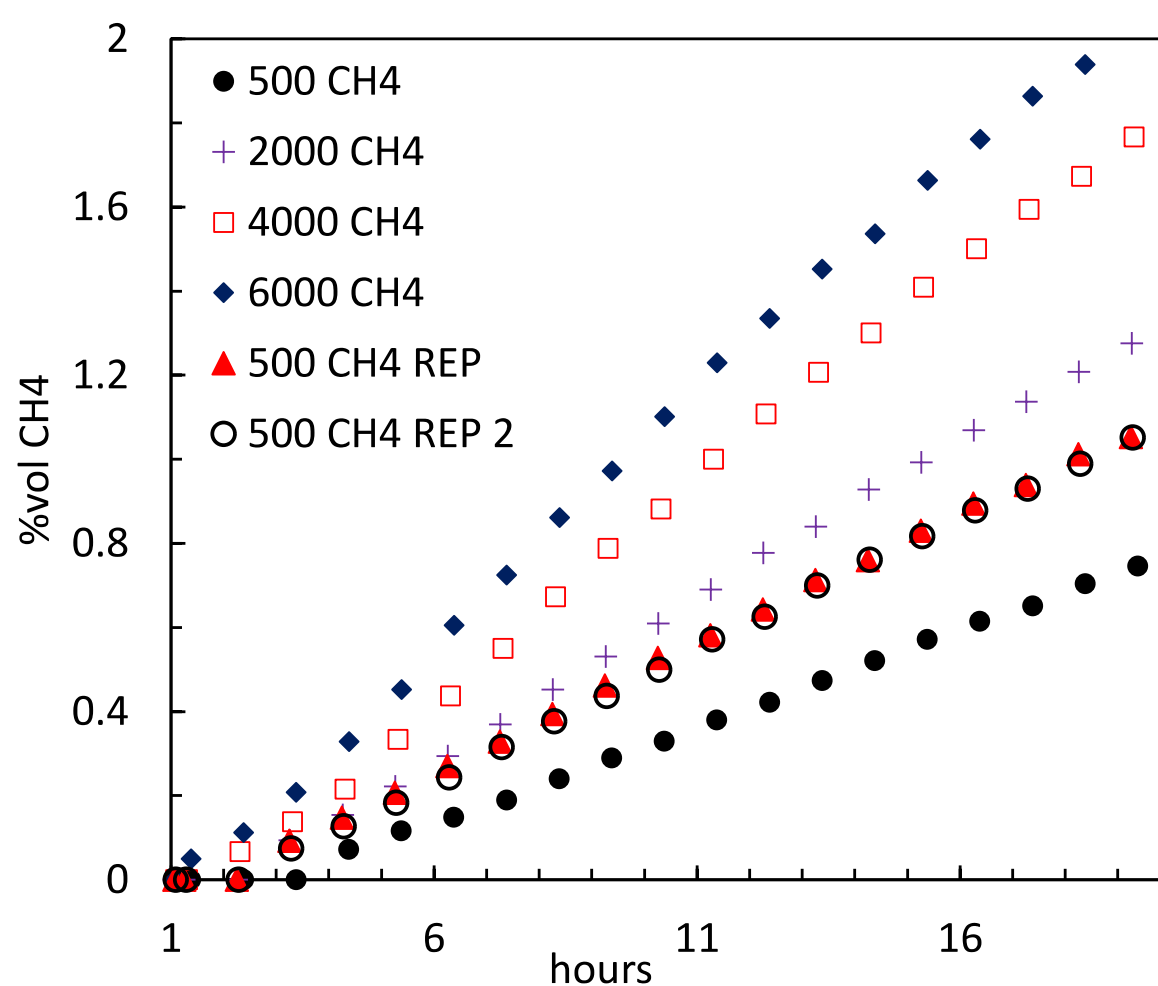


Figure 14 Methane progression through the first 24 hours of experiment

To obtain the yields and the efficiency the calculation process mentioned on equations 4.4.1 and 4.4.2 is repeated in the same manner as in section 5.1.1, obtaining the values reported on the Table 4. The first conclusion that it is possible to make is the noticeable effect of the pump flow rate and thus the residence time on both the yield and the

overall efficiency of the process, hence, is it feasible to assume that although the reaction is severely thermodynamically limited, the reaction kinetics are fast enough to increase the methanol production with the reduction of the gases' residence time.

As well as it was pointed out on 5.1.1, there is still no clear correlation between the CO plateau and the methanol yield or the efficiency of the process, for the production is increased with the increasing flow rate as well as it does with the monoxide plateau, but there is still a big difference in efficiency between the 6000 experiment and the 4000, even though they show the same maximum CO concentration, alternatively, the difference between the maximum CO concentration on all the 500 experiments is noticeable, yet the last 2 experiments present a greater yield and more efficiency.

The second noticeable effect regarding the Table 4 is the fact that exist a change on the catalyst reaction mechanism, due to the change between the CO concentrations on the 1st, 5th and 6th experiments, there is a difference of nearly 2% on the maximum amount of monoxide produced, still this fact doesn't seem to affect the reaction efficiency nor the yield, then it is a strong possibility to assume that during the reactions, due to the constant high temperature, pressure and the diffusion/adsorption of gases on the surface of the catalyst, the structure of it changes in some way that the reaction mechanism is different, but not less effective or efficient. Unfortunately, to prove this theory, it would be necessary to have complex studies of the spent catalyst, which are impossible to execute due to lack of equipment.

The procedure is repeated with 20wt.% obtaining consistent results, concluding that the reaction rate is fast enough to increase the overall conversion rate when the recycle rate is increased.

5.1.3. Catalyst degradation (20wt.% and 30wt.% Cu/MgO)

Although the experiment proved to produce satisfactory results, is equally important to achieve the reproducibility of the catalyst, since a one-use catalyst has little to no use in a real environment. For this to happen, the experiment is conducted sequentially, comparing the experiment results to each other, until the result is constant, determining the deactivation rate of the catalyst and the base or deactivated performance of it.

The degradation was assessed with 30 and 20 weight percent Cu/MgO catalyst since both show remarkably close satisfactory results on the previous experiments. The obtained results are presented in Figure 15, Figure 16, Table 5 and Table 6.

Table 5 Reproducibility results

Experiment	Catalyst	Hours	Avg reflux	Actual pressure	Product Vol	MeOH	wt.% MeOH	Yield	Efficiency
		[h]	[ml/min]	[bar]	[ml]	[g]	[%]	[%]	[gMeOH/h]
30wt.% REP 1	30wt.% Cu/MgO 550°C	24.07	3941.5	45	44.25	32.44	0.47	66.29%	0.63
30wt.% REP 2	30wt.% Cu/MgO 550°C	24.08	3991.3	45	44.43	29.36	0.469	67.07%	0.57
30wt.% REP 3	30wt.% Cu/MgO 550°C	24.07	*	45	*	26.22	0.466	*	0.51

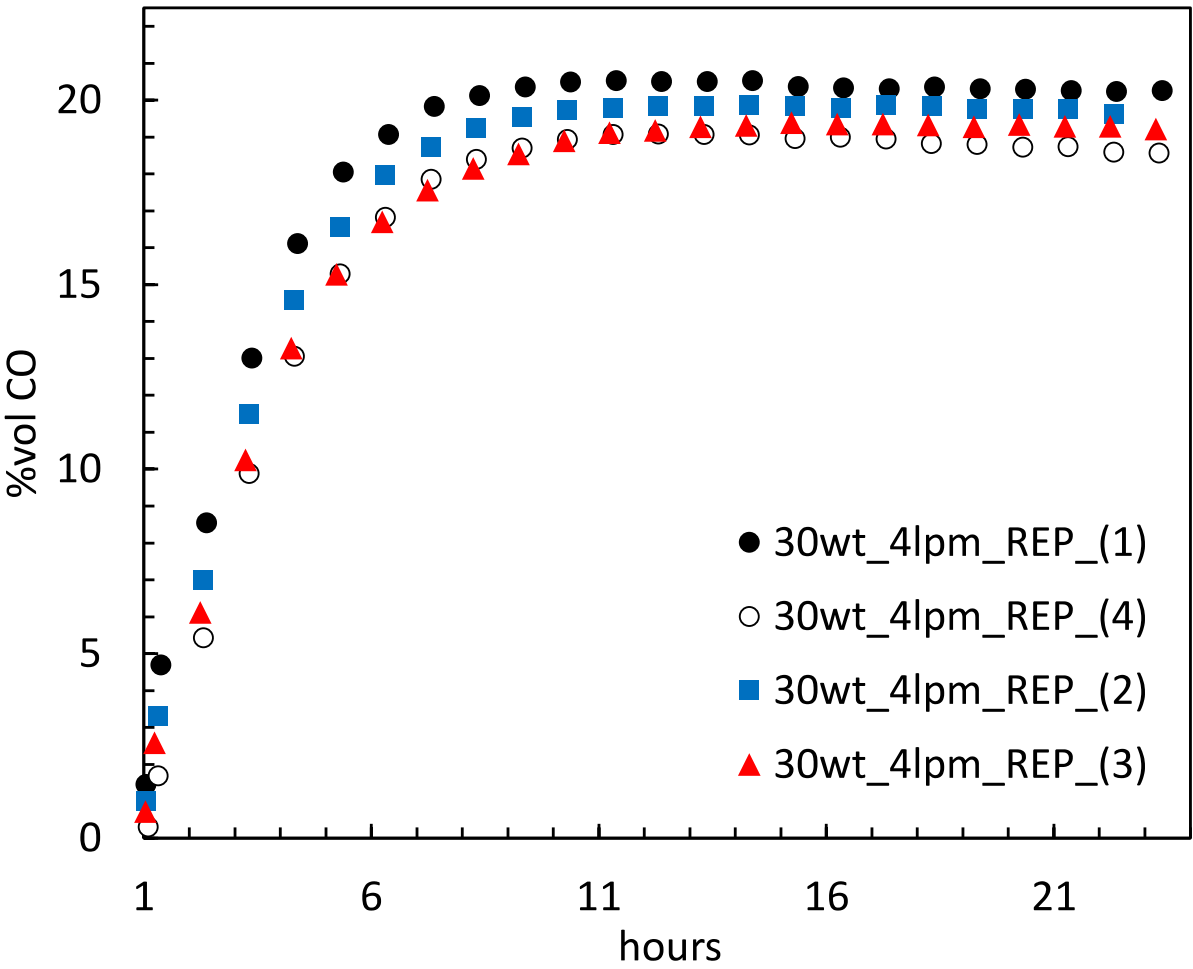


Figure 15 CO time progression for 30wt.% reproducibility

*Due to a problem with the program and the bottle mixture, some data was lost from the last experiment, and the 4th repetition could not be conducted at the desired pressure.

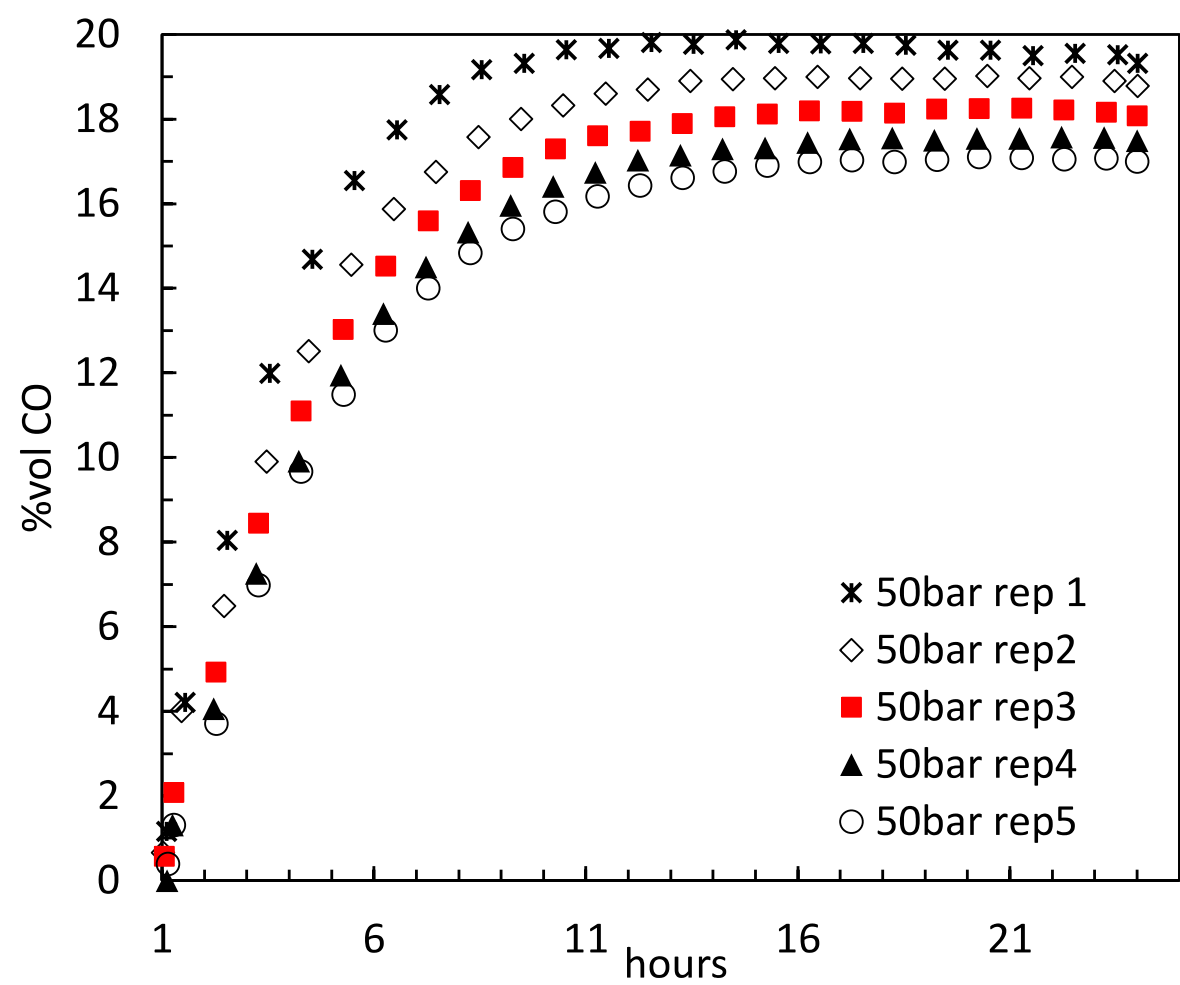


Figure 16 CO time progression for 20wt.% reproducibility

Table 6 20 wt.% 50 bar reproducibility

Experiment	Catalyst	Hours	Avg reflux	Actual pressure	Product wt.	MeOH	wt.% MeOH	Yield	Efficiency
		[h]	[ml/min]	[bar]	[g]	[g]	[%]	[%]	[gMeOH/h]
20wt.% 4000 50bar REP 1	20wt.% Cu/MgO 550°C	24.07	3964.1	49.616	31.74	14.37	0.453	62.86%	0.60
20wt.% 4000 50bar REP 2	20wt.% Cu/MgO 550°C	24.07	3985.5	49.446	30.30	13.55	0.447	67.56%	0.56
20wt.% 4000 50bar REP 3	20wt.% Cu/MgO 550°C	24.07	3974.1	50.155	27.21	12.17	0.447	62.86%	0.51
20wt.% 4000 50bar REP 4	20wt.% Cu/MgO 550°C	24.07	3859.2	50.222	25.65	11.30	0.44	61.74%	0.47
20wt.% 4000 50bar REP 5	20wt.% Cu/MgO 550°C	24.07	3998.3	49.744	23.52	10.49	0.446	60.08%	0.44

5.1.4. Catalyst degradation at 30 bar (30wt.% Cu/MgO)

Due to the bottle mixture running out of pressure, it was decided to do a 30-bar series of reproducibility experiments and testing at the same time the feasibility of the experiment at such a low pressure, the experiment is done consecutively, comparing the results to each other, and seeing if there's catalyst degradation. The obtained results are presented on Figure 17 and Table 7.

Table 7 experimental data from 30-bar reproducibility experiments

Experiment	Catalyst	Hours	Avg reflux	Actual pressure	Product Vol	MeOH	wt.% MeOH	Yield	Efficiency
		[h]	[ml/min]	[bar]	[ml]	[g]	[%]	[%]	[gMeOH/h]
30wt.% 4000 30bar REP	30wt.% Cu/MgO 550°C	24.07	3798.2	30	29.54	16.02	0.403	49.07%	0.27
30wt.% 4000 30bar REP 2	30wt.% Cu/MgO 550°C	24.07	3893.5	30	29.87	18.66	0.407	57.60%	0.32
30wt.% 4000 30bar REP 3	30wt.% Cu/MgO 550°C	24.07	4018.6	30	30.06	16.88	0.402	48.42%	0.28
30wt.% 4000 30bar REP 4	30wt.% Cu/MgO 550°C	24.07	4128.9	30	30.04	15.54	0.412	47.78%	0.27

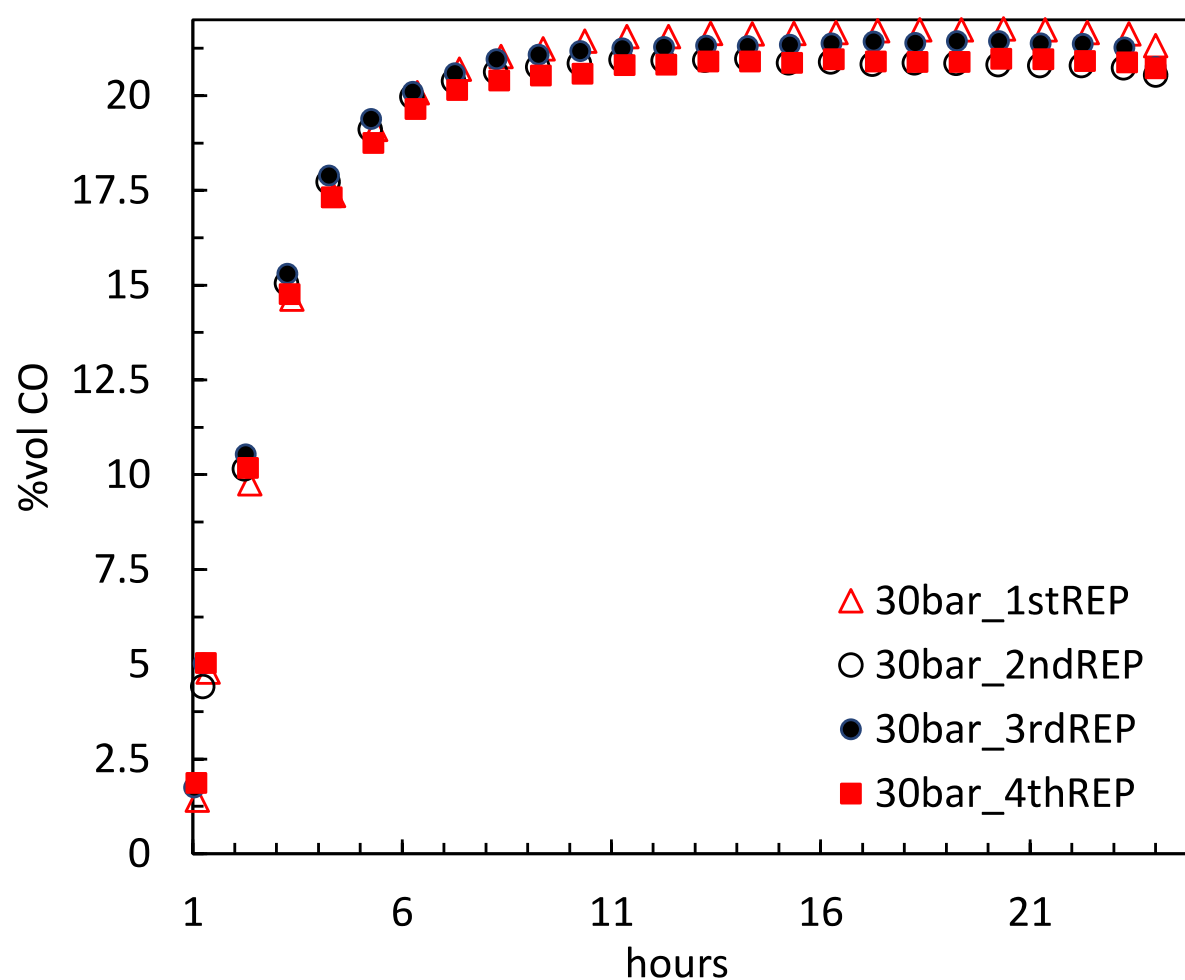


Figure 17 CO time progression for the reproducibility at 30 bar

Is possible to observe that there is no evidence of catalyst deactivation or degradation during the experiments when they are performed at 30 bar, nevertheless, the yields and the efficiency of the reaction is dramatically reduced, barely reaching 40% of the efficiency obtained at 50 bar.

This is possible to explain due to the reverse water gas shift reaction performing better at low pressures, but the volume negative reaction of methanol and water formation, is severely diminished when the pressure is reduced, increasing the CO equilibrium percentage, but reducing the amount of gas reacted into methanol.

5.1.5. High temperature series (20wt.% Cu/MgO)

After the experiments performed, it has been proven that there is some catalyst degradation when the experiment is done at 50 bar but is at that pressure when the high efficiencies are achieved, while the 30-bar series of experiments, does not show appreciable degradation, but the efficiency of the reaction is not even near satisfactory. To eliminate, or reduce the catalyst degradation as much as possible, the following questions were asked; *¿What is changing on the reaction between one experiment and the following one?* And more importantly *¿Is there a possibility to modify the system to eliminate this changes?*

Since the experiments conducted on 5.1.1 showed that the catalyst is able to function on a consistent efficiency and stability for longer than 24 hours, there is three main issues that can possibly be affecting the catalyst activity, the heating up and cooling down of the system between each one of the repetitions, the pressure and depressurization of the system between experiments, or the intrinsic fact of the reaction starting over again altering the characteristics of the catalyst. While the first two are controllable, if the third one was the reason of why the results were not consistent, then the catalyst would not fit for a real-life process for it is necessary to be able to run multiple cycles of reaction, but the pressure and the temperature is controllable and there is the chance of modifying the sequence of the experiment to evaluate this parameter.

The equipment for the reactor did not allow to keep the pressure high between the extraction of the product and the re-assembly of the system, since it is necessary to open the system to take out the liquid product from the product vessel and evaluate the efficiency of the reaction, nonetheless it is possible to keep the temperature high

and taking out the product keeping the whole reactor at 300°C. Therefore, the sequence of making the reproducibility experiments, was changed to a new one, where the system is first heated up to 300°C, then pressurized up to 50 bar, and after 22 hours, the product is taken without a cool down of the system but only a depressurization, hoping that this way would at best eliminate the catalyst degradation or at worst decrease it. This new series of experiments was identified with the tag “*HighT REP*” due to it being a reproducibility series where the system was consistently at a temperature of 300°C. The results of this series are presented on Table 8 and Figure 18.

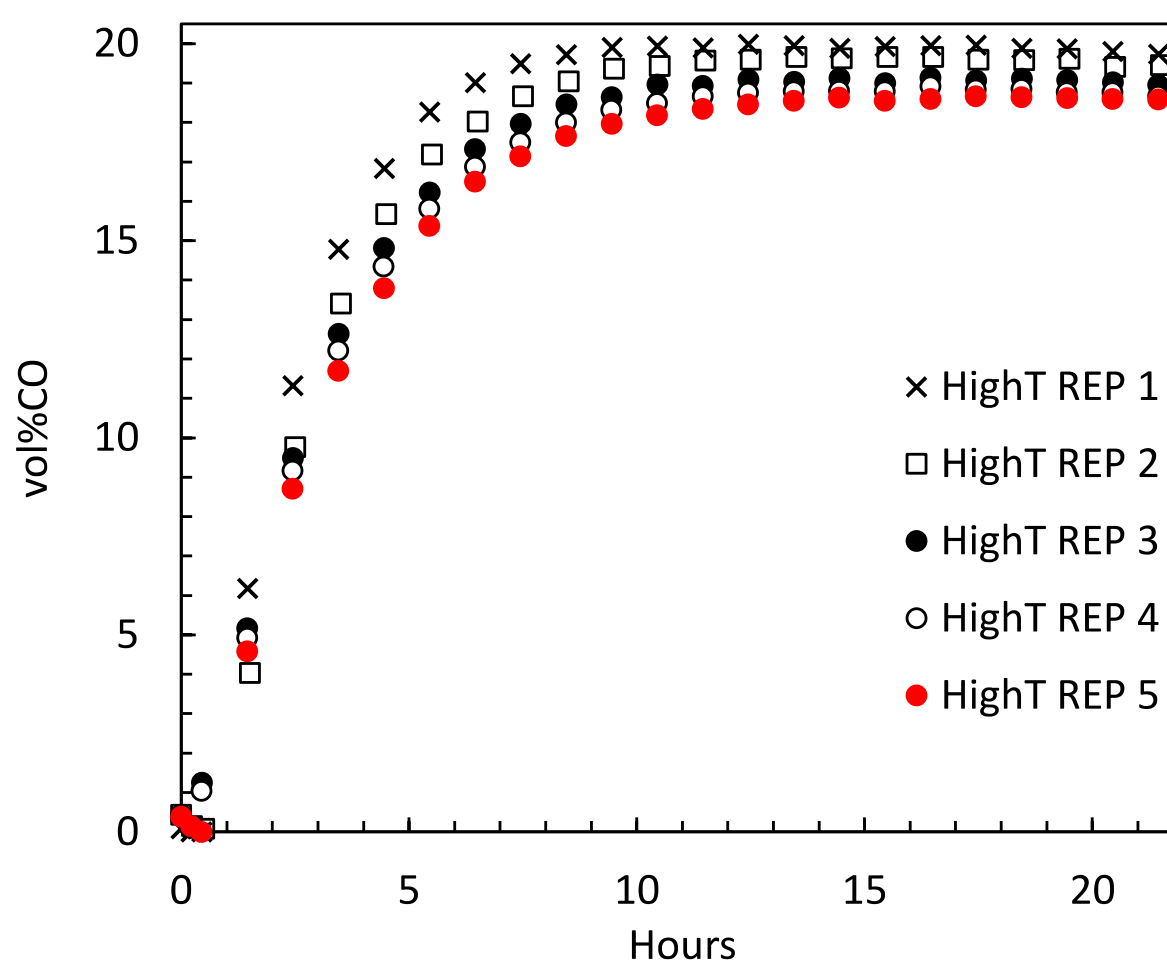


Figure 18 CO progression along the HighT reproducibility series

Table 8 HighT reproducibility results

Experiment	Catalyst	Hours	Avg reflux	Actual pressure	Product wt.	MeOH	wt.% MeOH	Yield	Efficiency
		[h]	[ml/min]	[bar]	[g]	[g]	[%]	[%]	[gMeOH/h]
20wt.% HighT REP 1	20wt.% Cu/MgO 550°C	22.07	3950.9	50.028	37.51	17.96	0.479	76.09%	0.81
20wt.% HighT REP 2	20wt.% Cu/MgO 550°C	22.07	3990.1	50.708	29.37	14.04	0.478	65.37%	0.64
20wt.% HighT REP 3	20wt.% Cu/MgO 550°C	22.07	3970.6	50.733	31.93	14.95	0.468	73.57%	0.68
20wt.% HighT REP 4	20wt.% Cu/MgO 550°C	22.07	4066.2	50.756	30.93	14.50	0.469	73.21%	0.66
20wt.% HighT REP 5	20wt.% Cu/MgO 550°C	22.07	4190.7	50.898	30.57	14.29	0.468	72.61%	0.65

Looking at the values reported on Table 8, is possible to argue that the reproducibility of the experiment has been achieved with a small degradation observed after the first reaction but maintaining a constant yield, and efficiency with oscillations in the order of 1%, which are arguably result of outside parameters that may alter the measurements or the reaction itself and are not controllable.

Having achieved the reproducibility, then it is proven that the use of the catalyst is feasible for a real-life industrial process, proceeding with the results discussion.

6. Result analysis and discussion

On this section the results presented from 5.1.1 to 5.1.5 will be analyzed and compared to conclude on regard of the objectives of finding the optimal copper loading, the best process conditions and achieving the reproducibility of the experiment.

6.1. Optimal copper loading

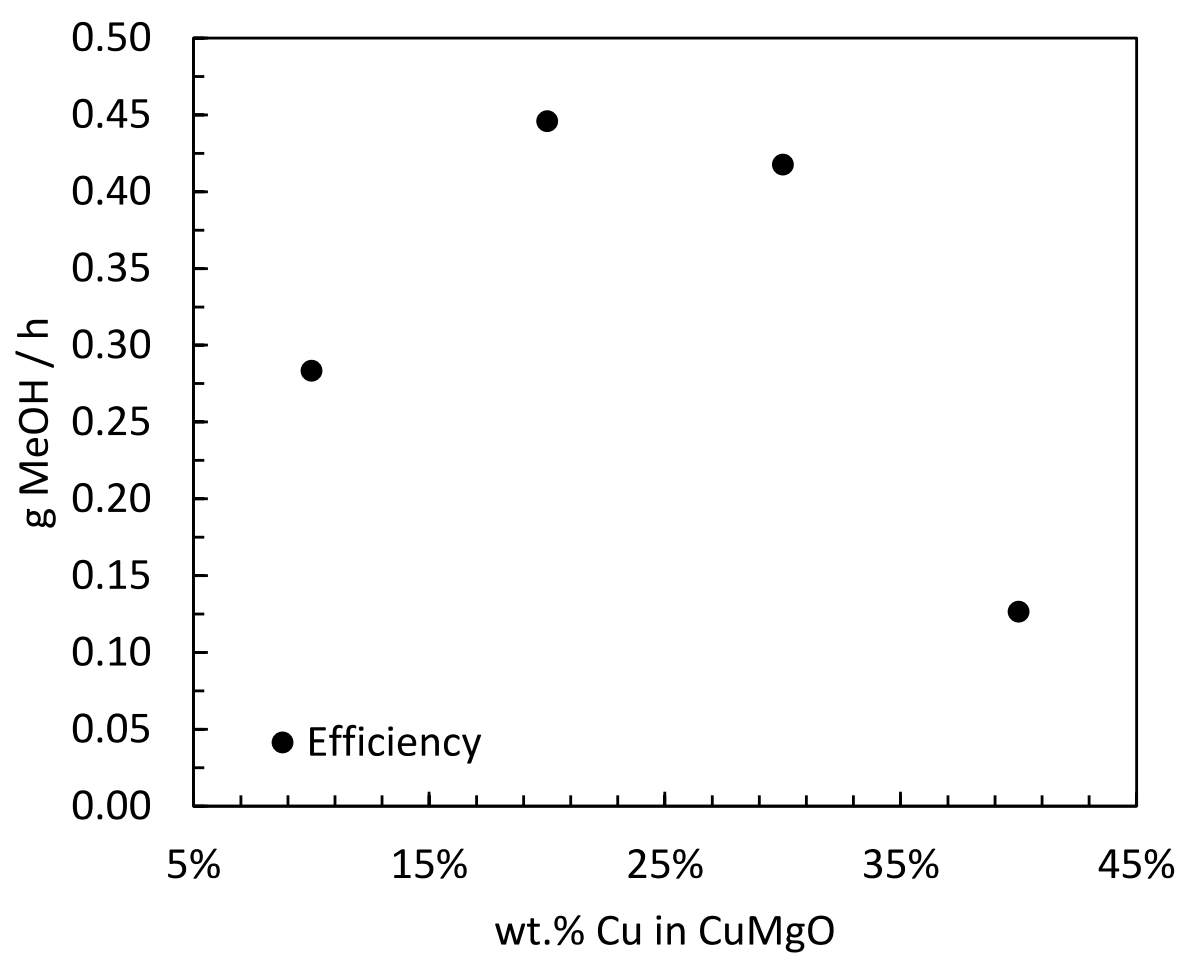


Figure 19 Catalyst Cu loading efficiency comparison

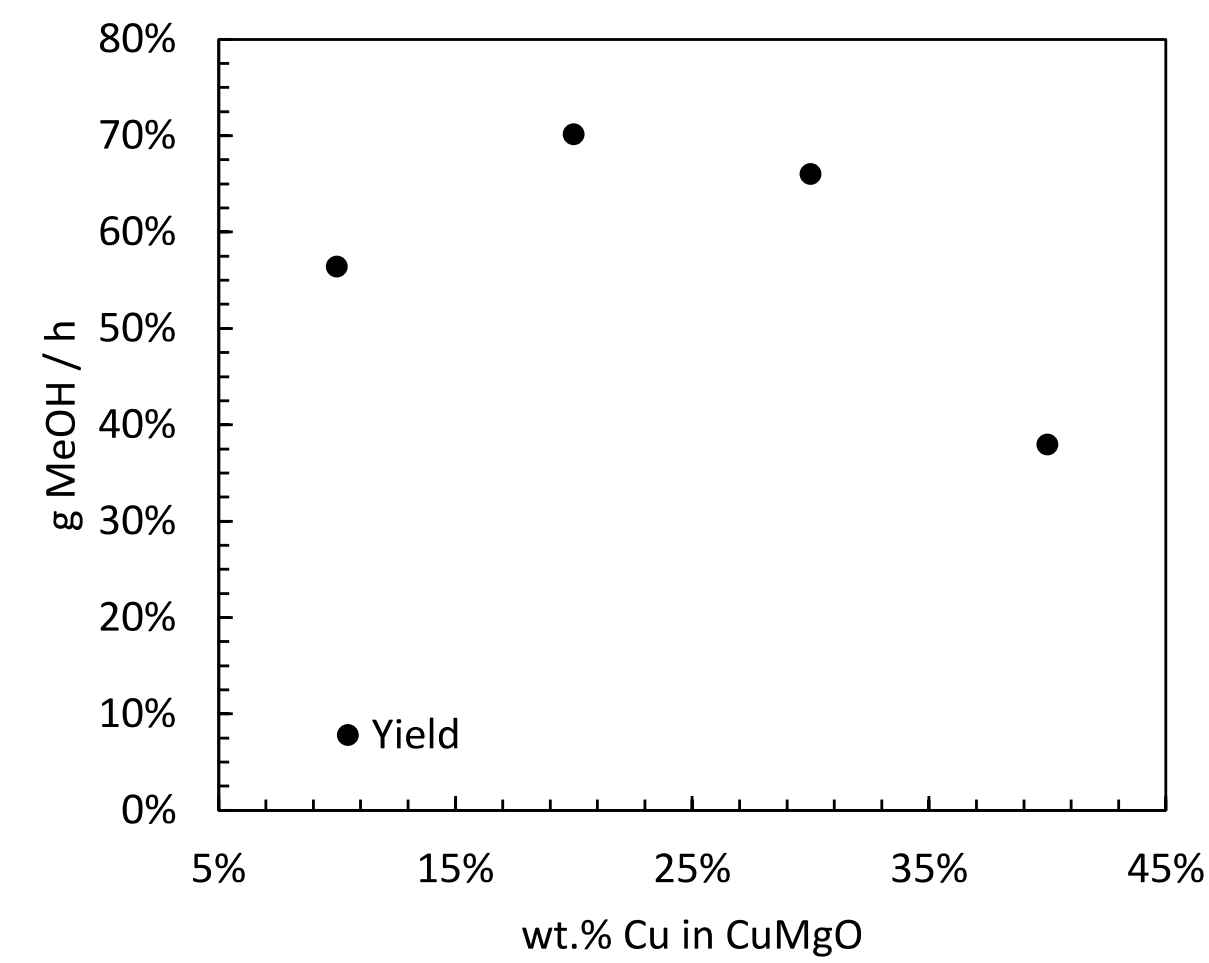


Figure 20 Catalyst Cu loading yield comparison

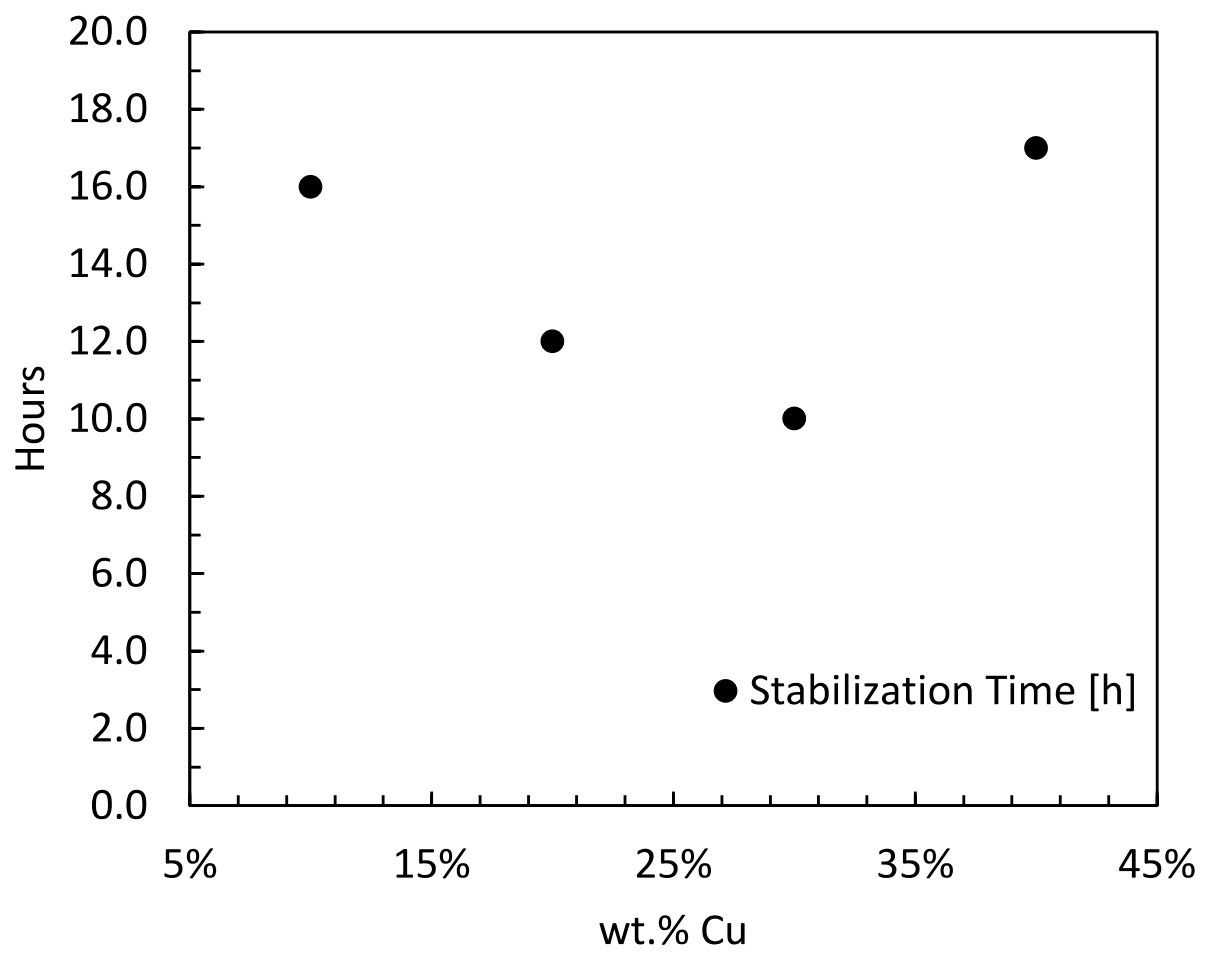


Figure 21 Cu loading comparison for the stabilization time

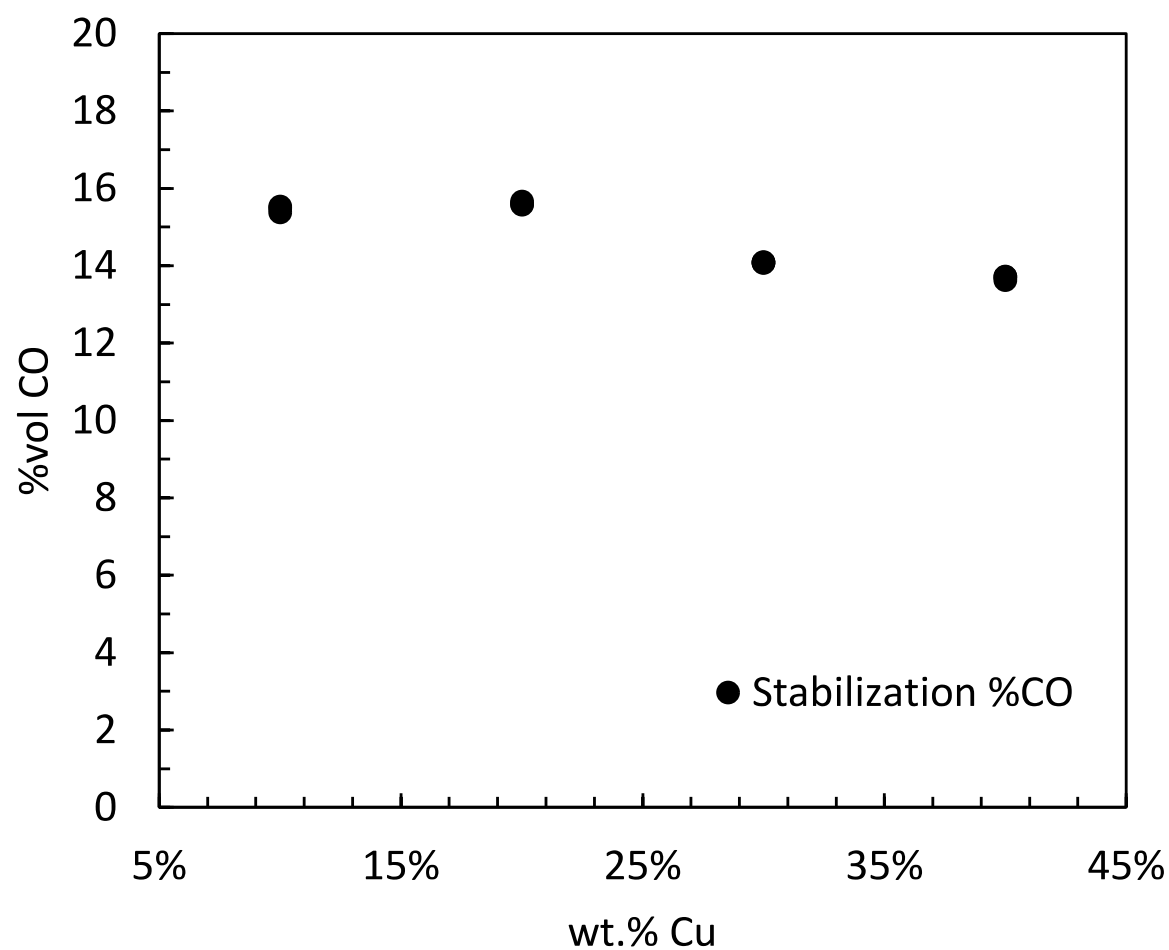


Figure 22 Cu loading comparison for the stabilization %CO

Analyzing the obtained data presented in the Figure 19 to Figure 22, it is possible to conclude that within the experiments realized, the best copper loading for both yield of CO_2 conversion as well as overall hourly methanol production is between 20wt.% and 30wt.%, with the first one showing better results in the reaction rate and efficiency, while the later showing advantage in the stabilization time.

6.2. Circulating load configuration

The obtained results for the circulating load configuration, are presented on Figure 23 to Figure 26

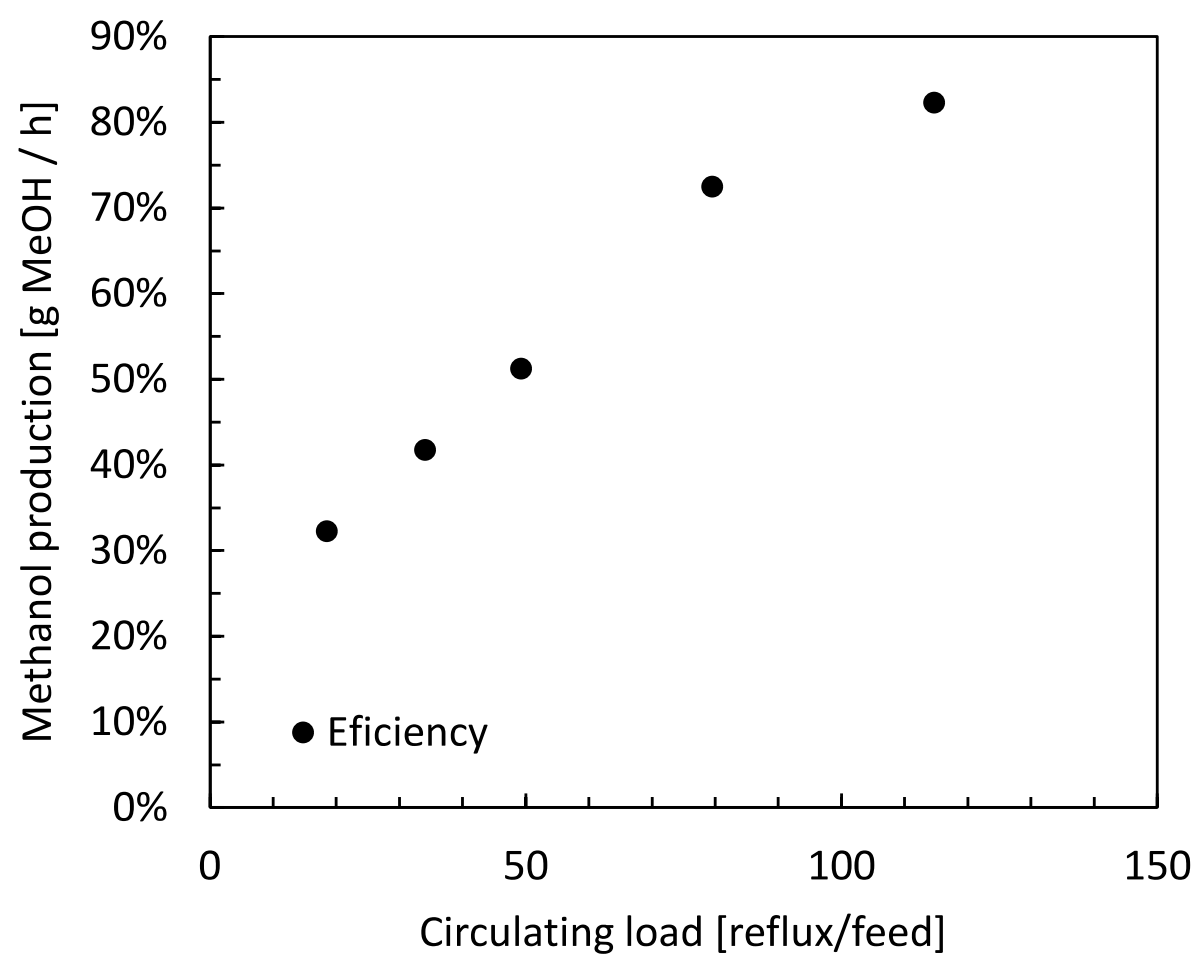


Figure 23 Circulating load effect over the efficiency of the reaction.

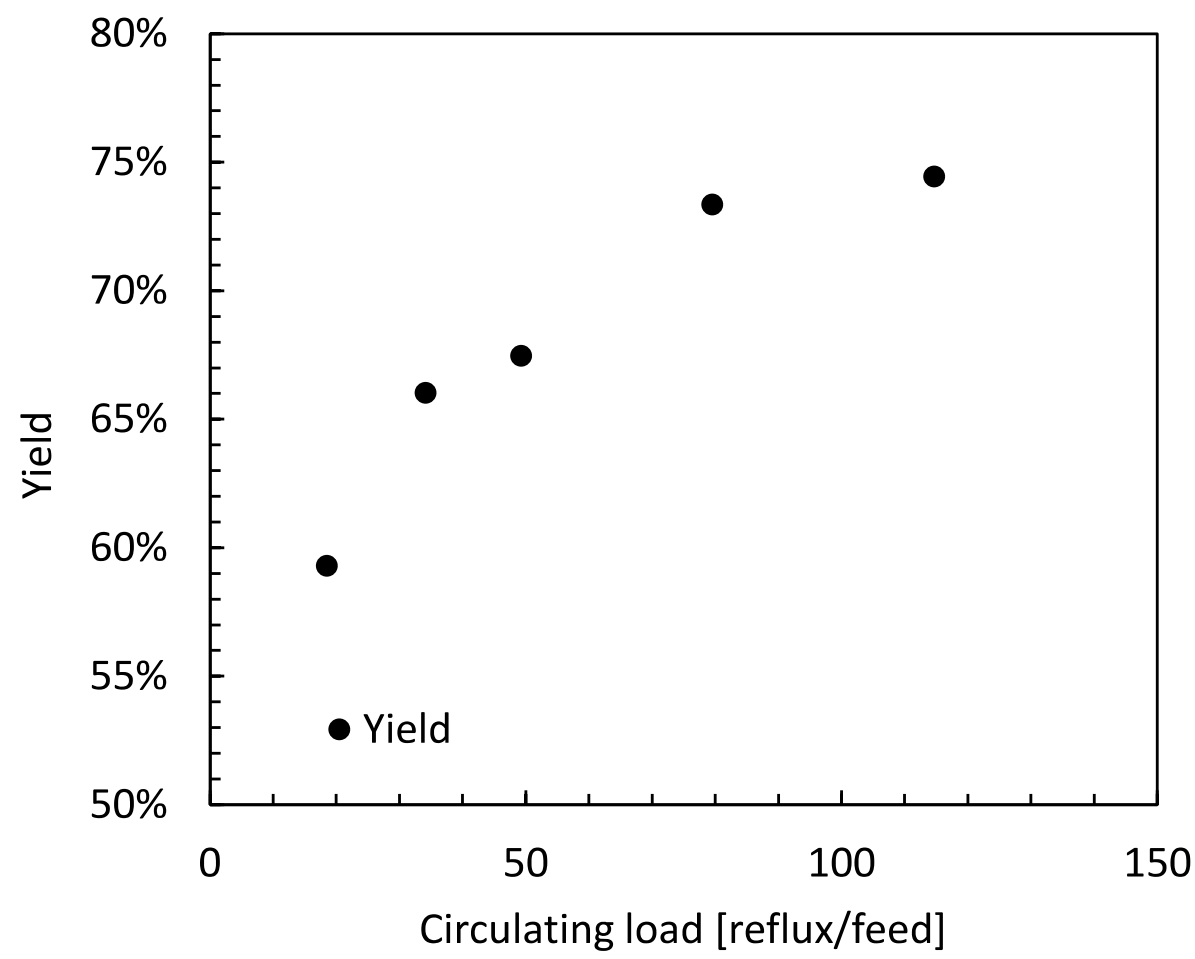


Figure 24 Circulating load effect over the yield of reaction.

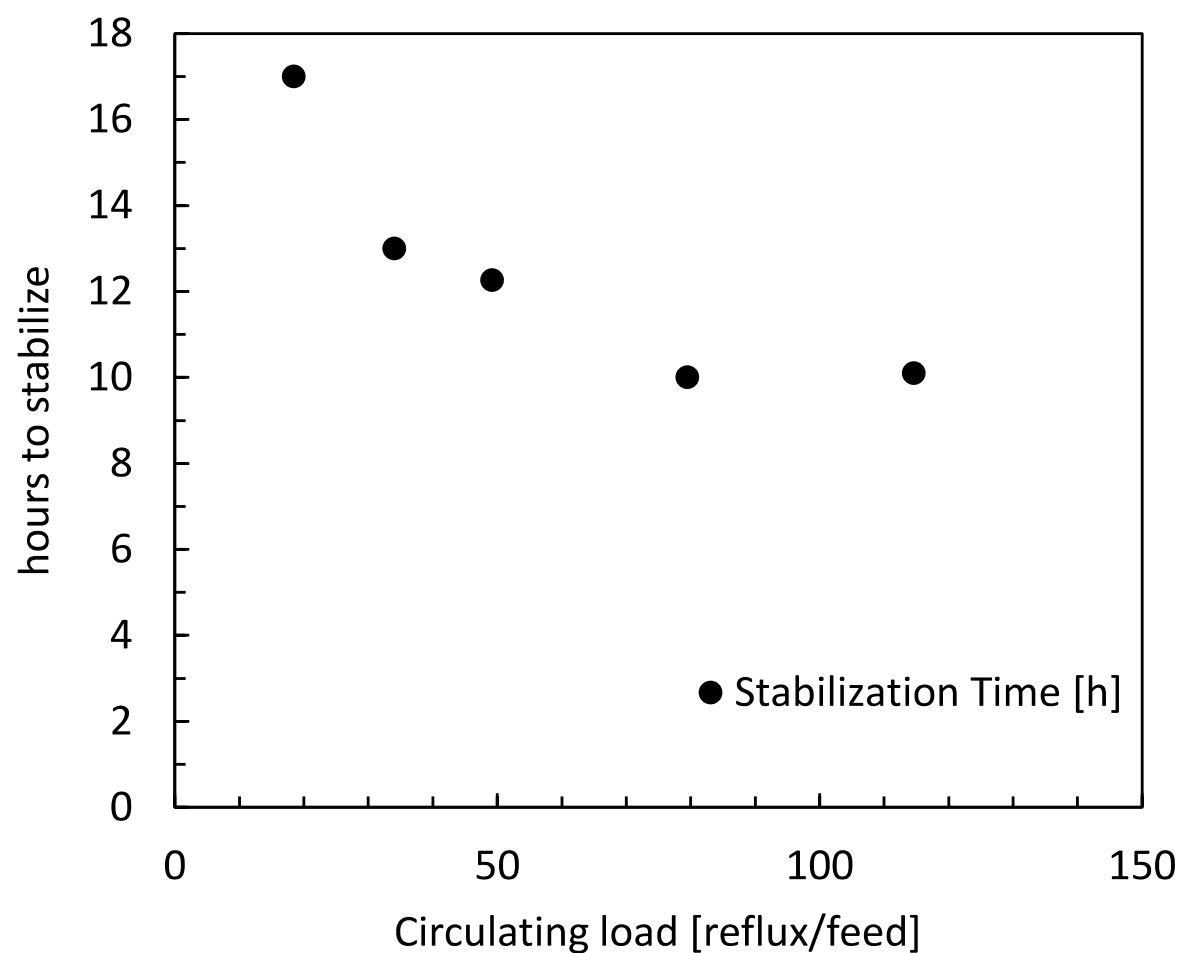


Figure 25 Circulating load effect for the stabilization time.

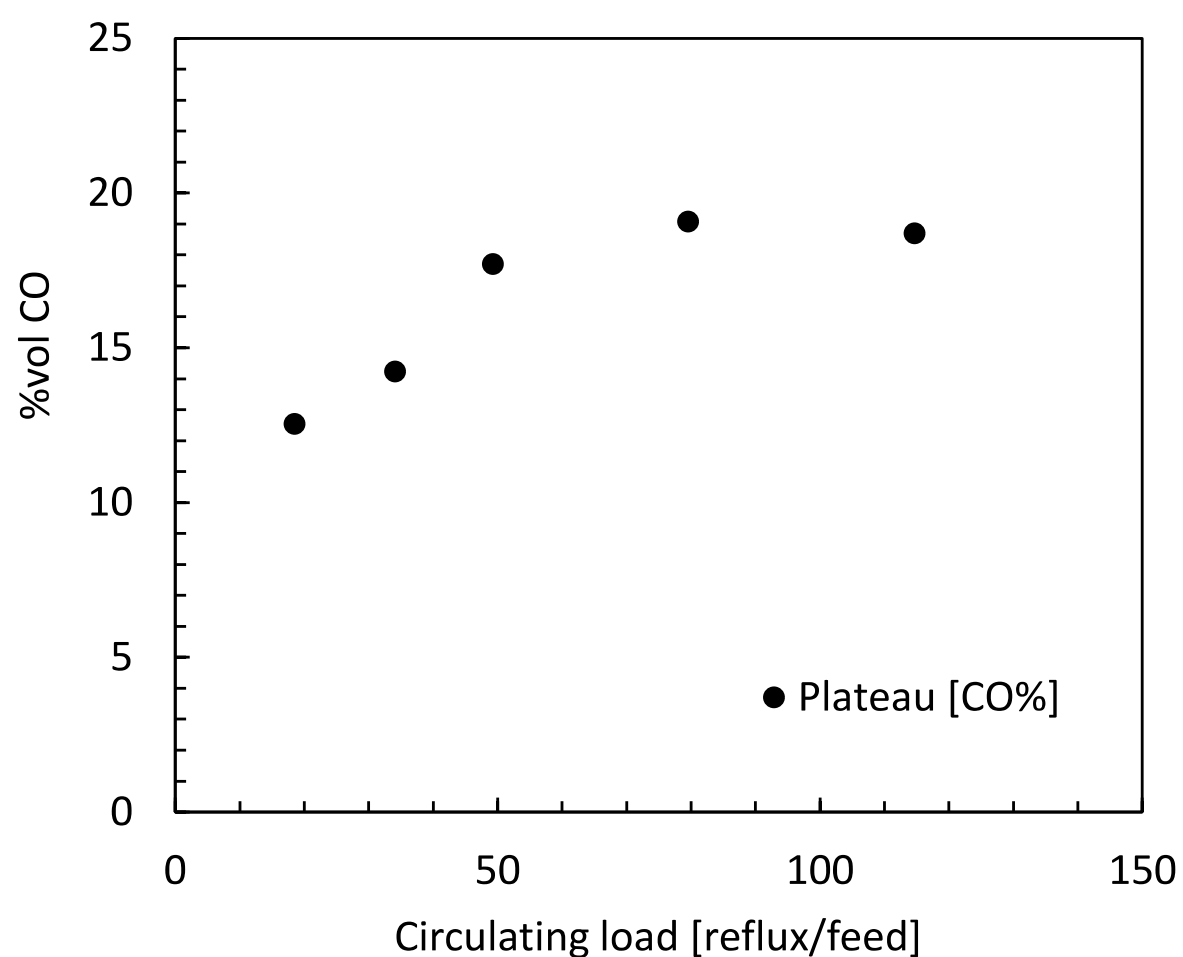


Figure 26 Circulating load effect for the stabilization %CO.

It is noticeable that, for one exact same catalyst, the pump flow rate affects directly and significantly on both the yield and the efficiency of methanol production as well as it does over the stabilization time and the maximum monoxide achieved, this could be explained due to a fast reaction rate but easily limited, so for faster extraction of the product, faster the reaction. It is necessary to further assess even greater pump flows,

since the reactor configuration did not have any mechanism to prevent catalyst flush away, the experiments were stopped at 6000 [Nml/min] but is likely that greater flows with a fixed catalyst configuration can improve the efficiency of even higher. It is also important to note that the yield increases slightly with the augment in the flow, but it seems to reach a plateau under 75%.

6.3. MgO calcination temperature

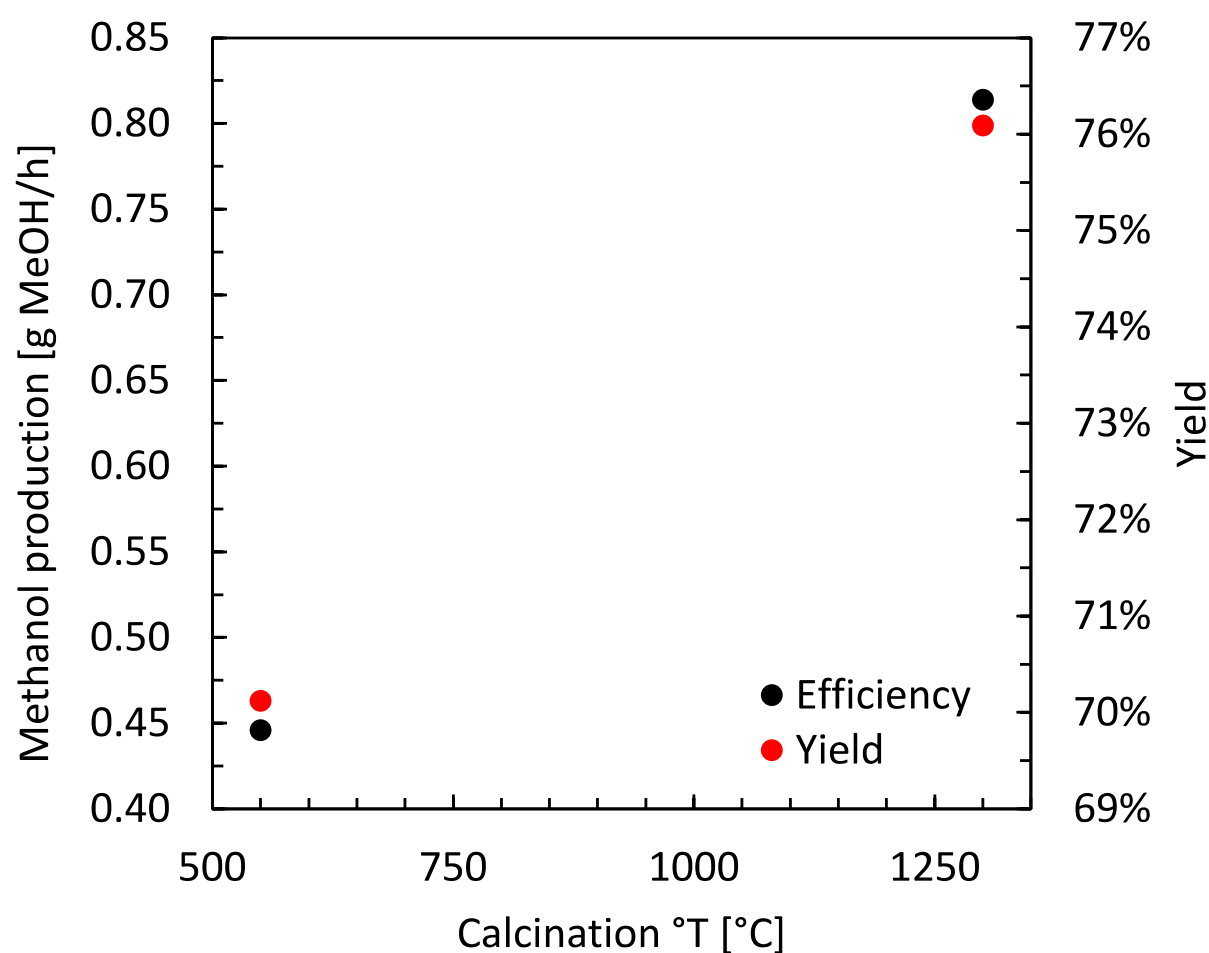


Figure 27 Calcination temperature results

Although only were evaluated two different calcination temperatures (Figure 27), there is a clear benefit observed when changing the temperature for the calcination of the magnesium carbonate to magnesium oxide. This is explicable by the fact that has been already studied in literature by Lux et al.[40], where the caustic properties of the magnesium oxide play a fundamental role in the hydrogenation reaction from magnesium copper catalysts and is known that the properties of the magnesium oxide are heavily modified by the calcination time and temperature, generating the different types of magnesium oxide, commonly known as caustic, sintered and dead-burnt magnesia[41].

6.4. Operation pressure

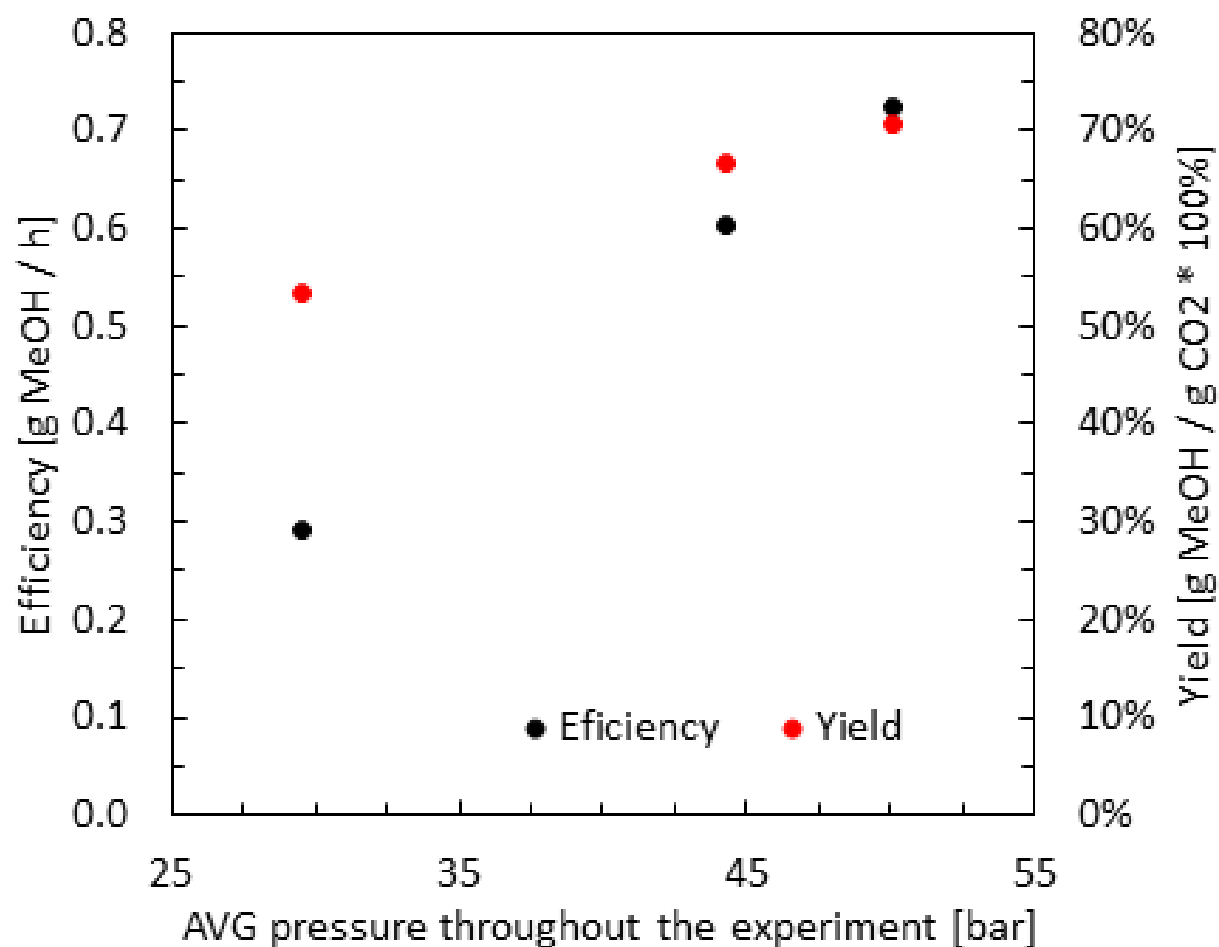


Figure 28 system operating pressure comparison

Analyzing the data presented in Figure 28, it can be concluded that both efficiency and yield of reaction are severely improved by the increase in the operating pressure of the system. Again, as shown in 6.2, it is likely that both parameters improve at even higher pressure, but due to physical limitations with the reactor, this could not be evaluated in this experiment. It is important to note that both in the pressure comparison and the catalyst temperature of calcination, the stabilization parameters were not compared, this is mainly due to the fact that the amount of monoxide, for this experiments is strongly influenced by the pressure, showing that at a lower pressures the plateau of CO is considerably high due to the reaction being favorable at lower pressures, thus generating a big amount of CO and very slowly forming methanol.

6.5. Degradation

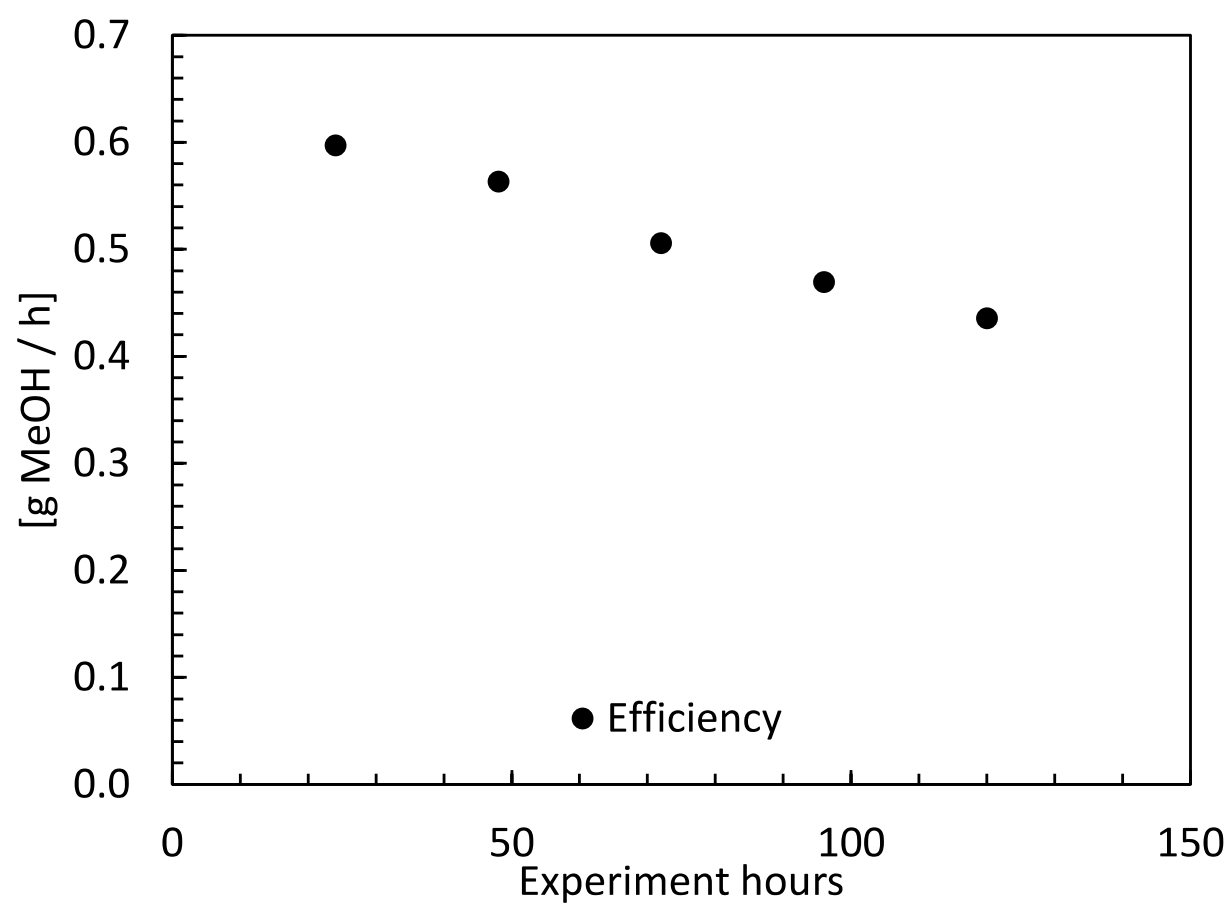


Figure 29 Degradation test efficiency results

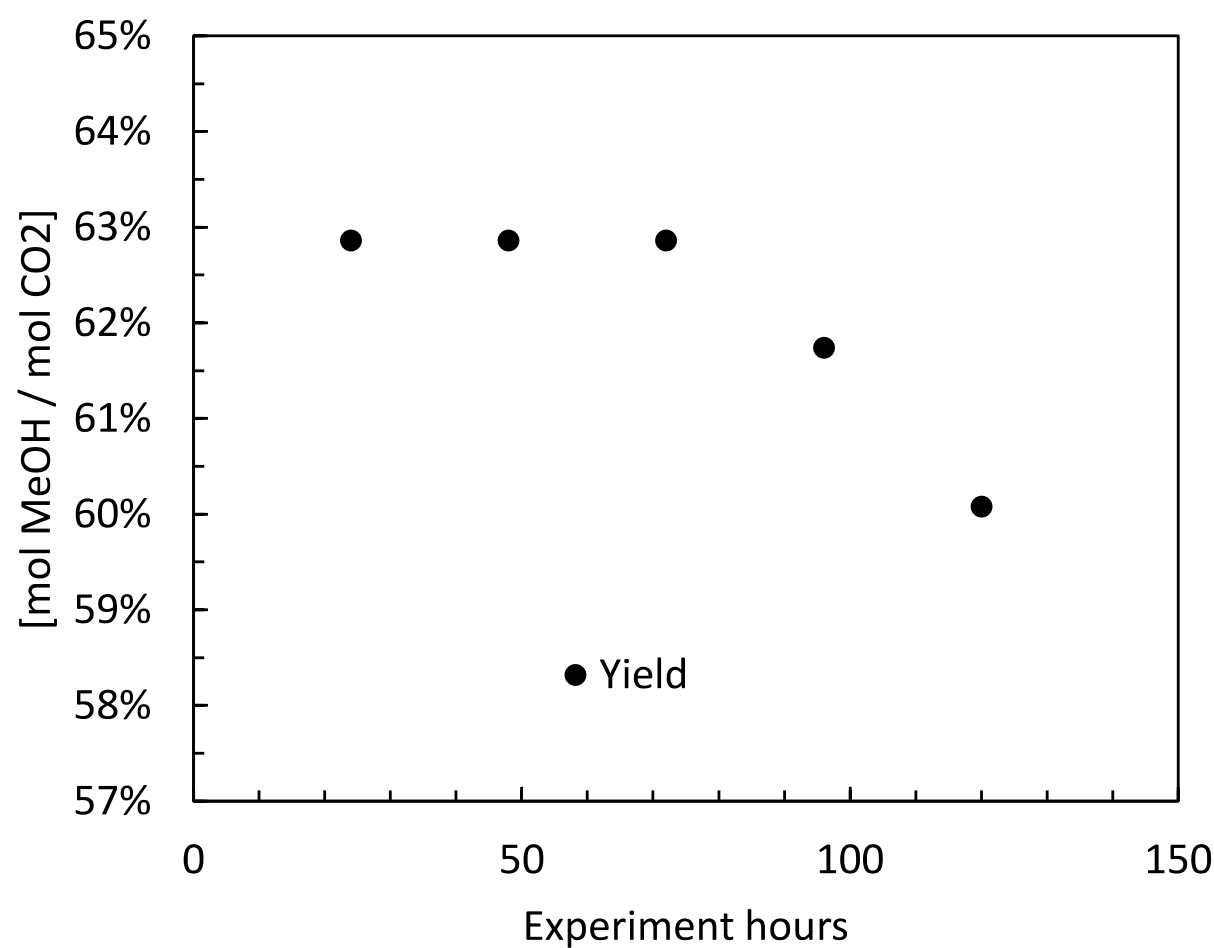


Figure 30 Degradation test Yield of reaction results

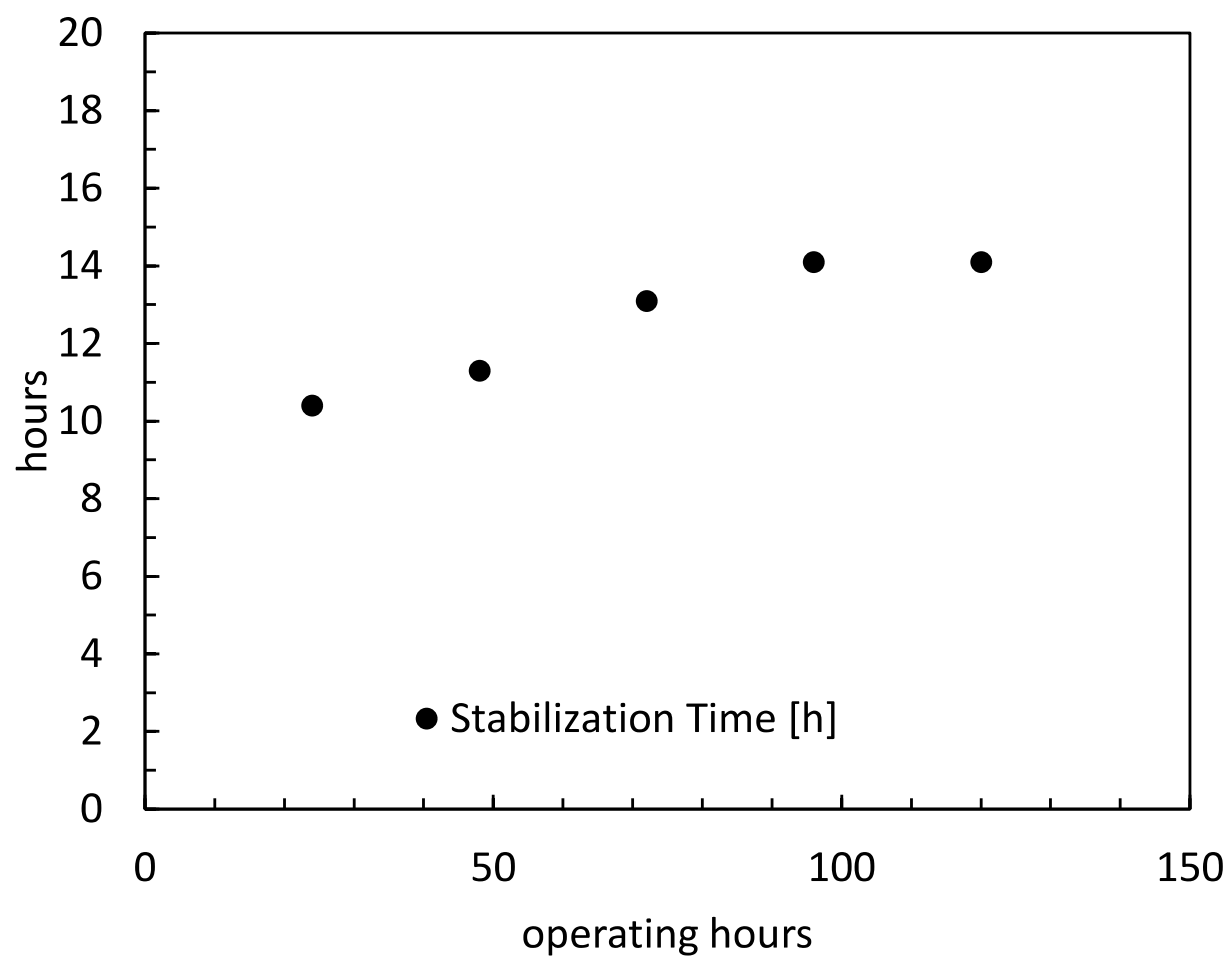


Figure 31 Degradation test results on stabilization time

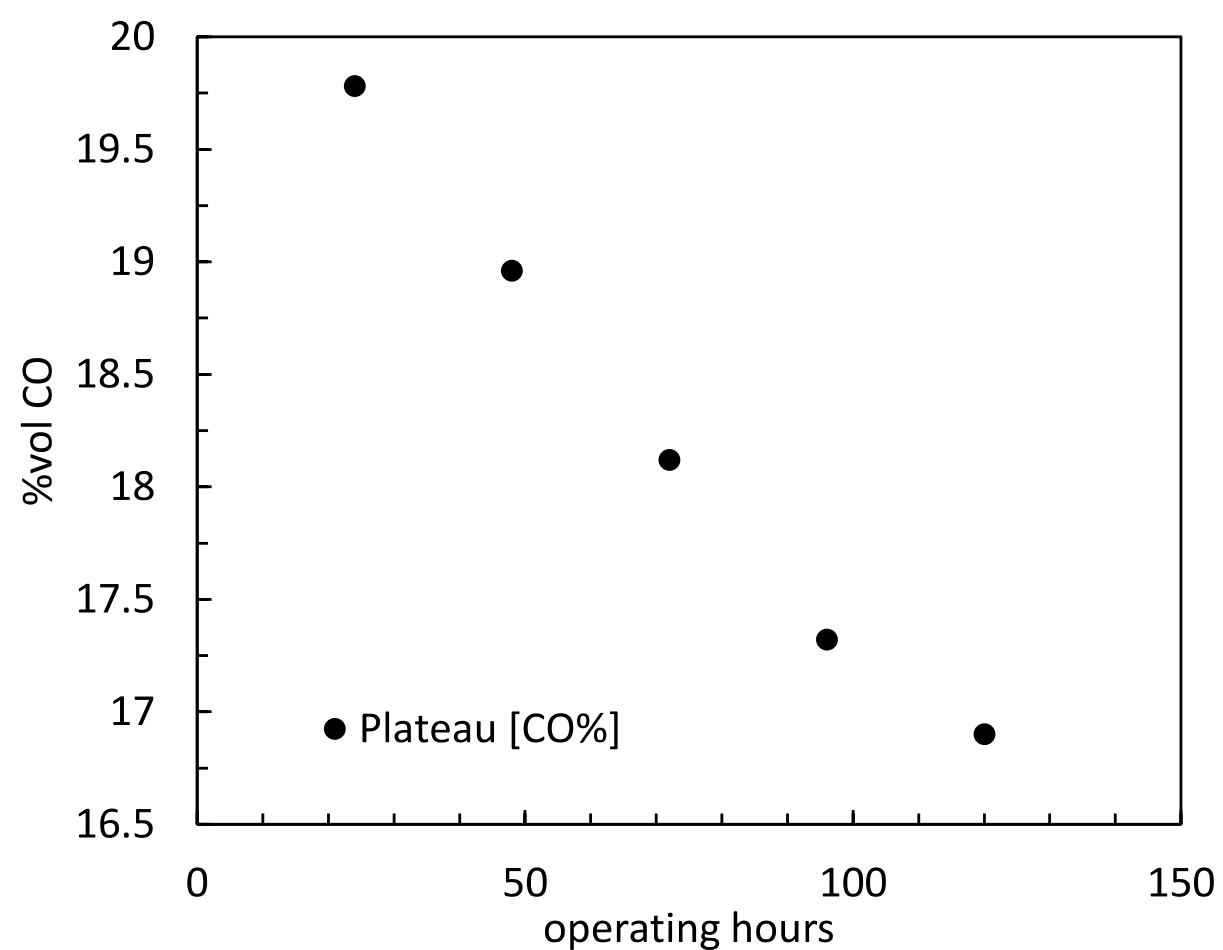


Figure 32 Degradation test results on stabilization %CO

It is possible to observe in Figure 30 that even though the yield of the reaction is kept constant, the efficiency (Figure 29) is declining at an almost constant rate, decreasing the catalyst activity on 1/3 of its original capacity, and since the main goal is to produce methanol, it is not satisfactory a decrease in the rate of production, even when the yield

is maintained. Unfortunately, it did not reach the point of minimum activity of the catalyst, so it is possible that at some point, after enough repetitions, the catalyst degrades completely, leaving very little or no noticeable activity. Regarding the stabilization parameters (Figure 31 and Figure 32), between the first and the 4th repetition the stabilization time increases in 40% which might be an indicator for why the efficiency decreases, since every experiment is fixed at 24h, each experiment “wastes” more hours in stabilizing, thus leaving less hours of pure production.

6.6. High T Degradation.

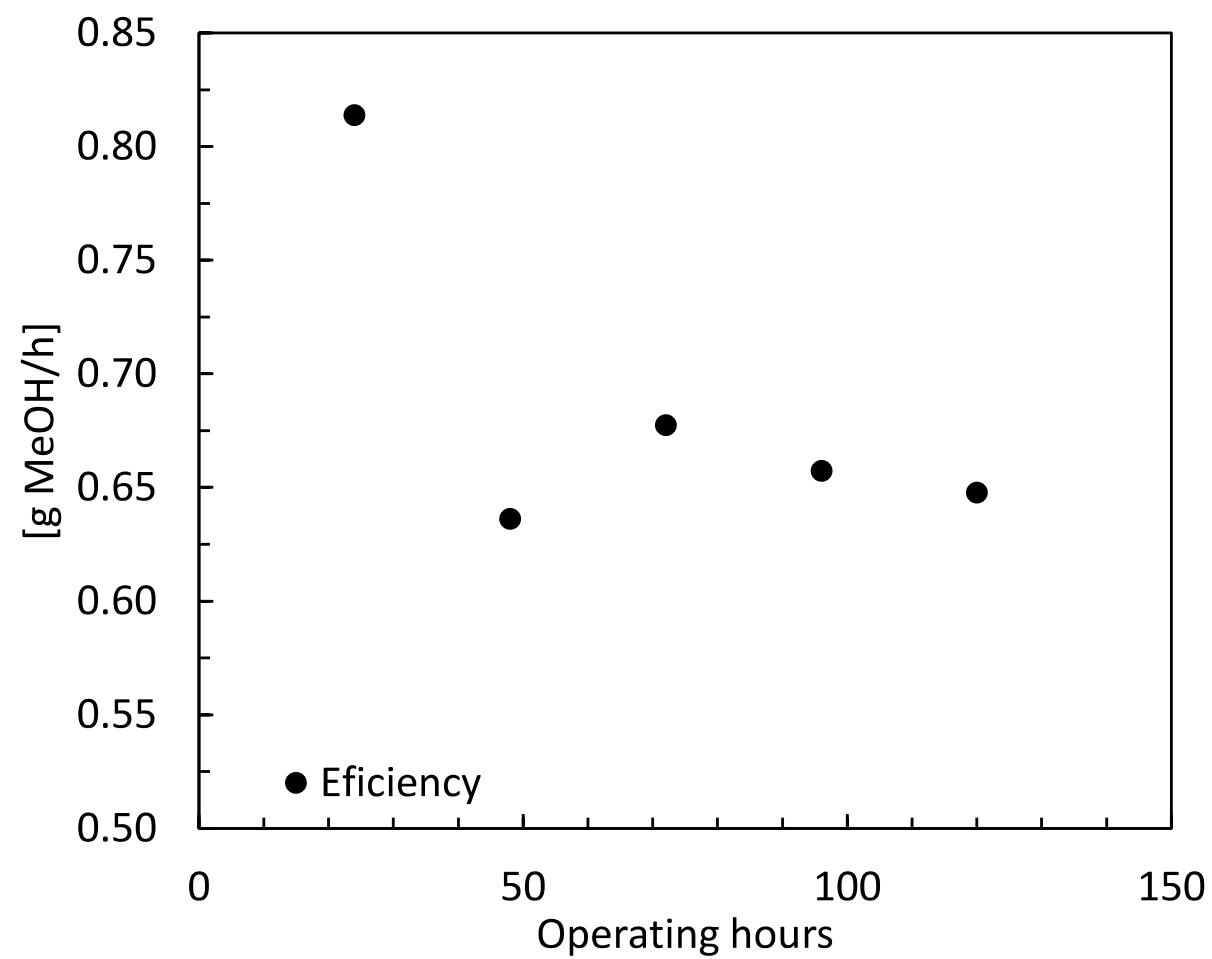


Figure 33 High Temperature degradation test efficiency

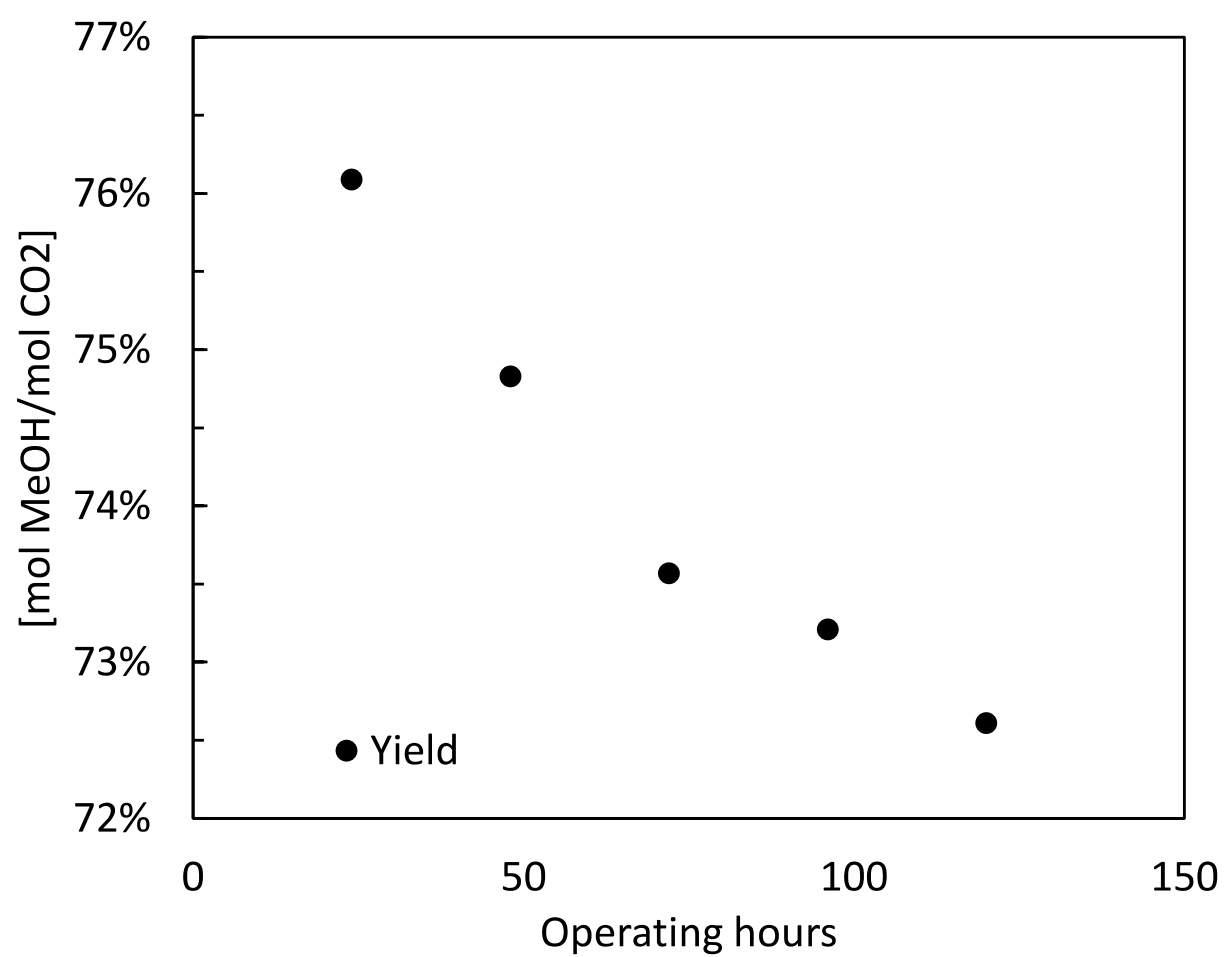


Figure 34 High temperature degradation test Yield

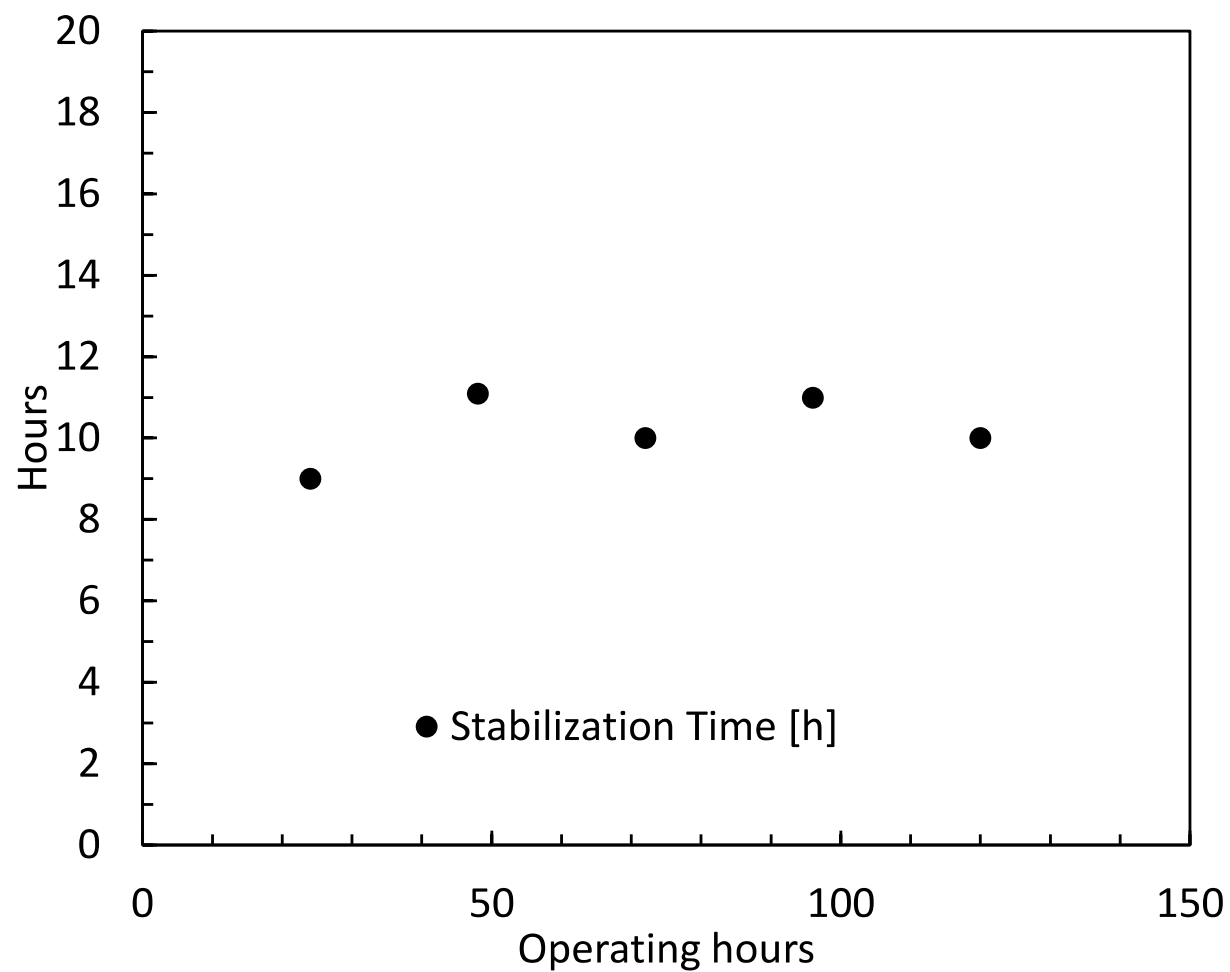


Figure 35 High Temperature comparison of stabilization time.

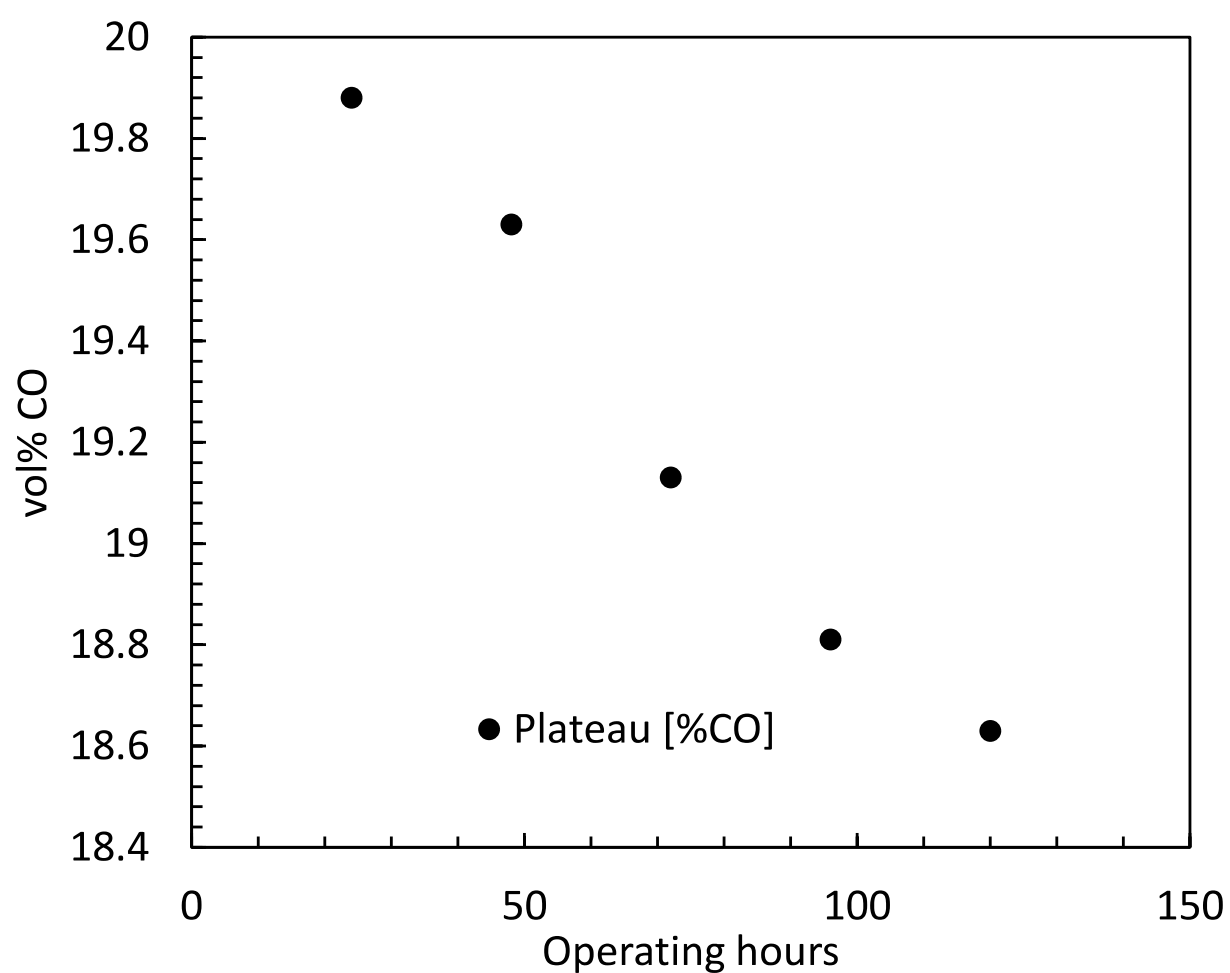


Figure 36 High Temperature comparison of stabilization %CO

It is possible to see that first, both indicators shown in Figure 33 and Figure 34 are highly influenced by the high temperature operation obtaining values well over the rest of all the other experiments, meaning that the heating up and cooling down cycle directly affects the catalyst characteristics and thus the efficiency, activity, yield. This could be explained possible deformations on the catalyst, considering that copper is a

highly sensitive to heat metal. The second fact that can be observed here is that although there is an initial degradation of the catalyst, experiencing a drop in the efficiency and the yield, from the second experiment onwards the indicators are maintained almost constant, and the differences observed between one and other are arguably oscillatory and due to small changes in the operation since is manually controlled, and thus very susceptible to small human errors, the stabilization times, seem to be maintained constant throughout the cycles as shown in Figure 35. Finally, it can be concluded that reproducibility is achievable with the copper magnesium catalyst if it is kept at reaction temperature. The equilibrium CO, although being constantly decreasing every cycle, it does not reach 1.5% difference over the span of 120h (Figure 36)

6.7. Model adjustment

In order to properly compare the experiments, and to obtain relevant information regarding the reaction, although it being composed of multiple smaller chain reactions that, for the purposes of this work, defining specific kinetic to each one of them is both virtually impossible and would not give a robust model, it is decided to define the whole reaction as one general big reaction process, where one kinetic constant value can represent the whole group. For this part of the study, the 50 bar degradation experiments are going to be assessed, to compare the effect of the degradation with each repetition.

The model selected for this reaction is given by the equation (6.7.1)

$$C_{CO}(t) = C_{\infty} \left(1 - e^{-k(t-t_0)^n}\right) \quad (6.7.1)$$

Where C_{∞} is the concentration of CO is the final concentration of CO, therefore the concentration at $t = \infty$, k is the kinetic constant of the reaction and n represents the factor determining the time limitations of the reaction, where $n < 1$ implies that the reaction is diffusion controlled.

Then, taking the data from 5.1.3, it is possible to adjust the reaction progress (Figure 37 to Figure 41):

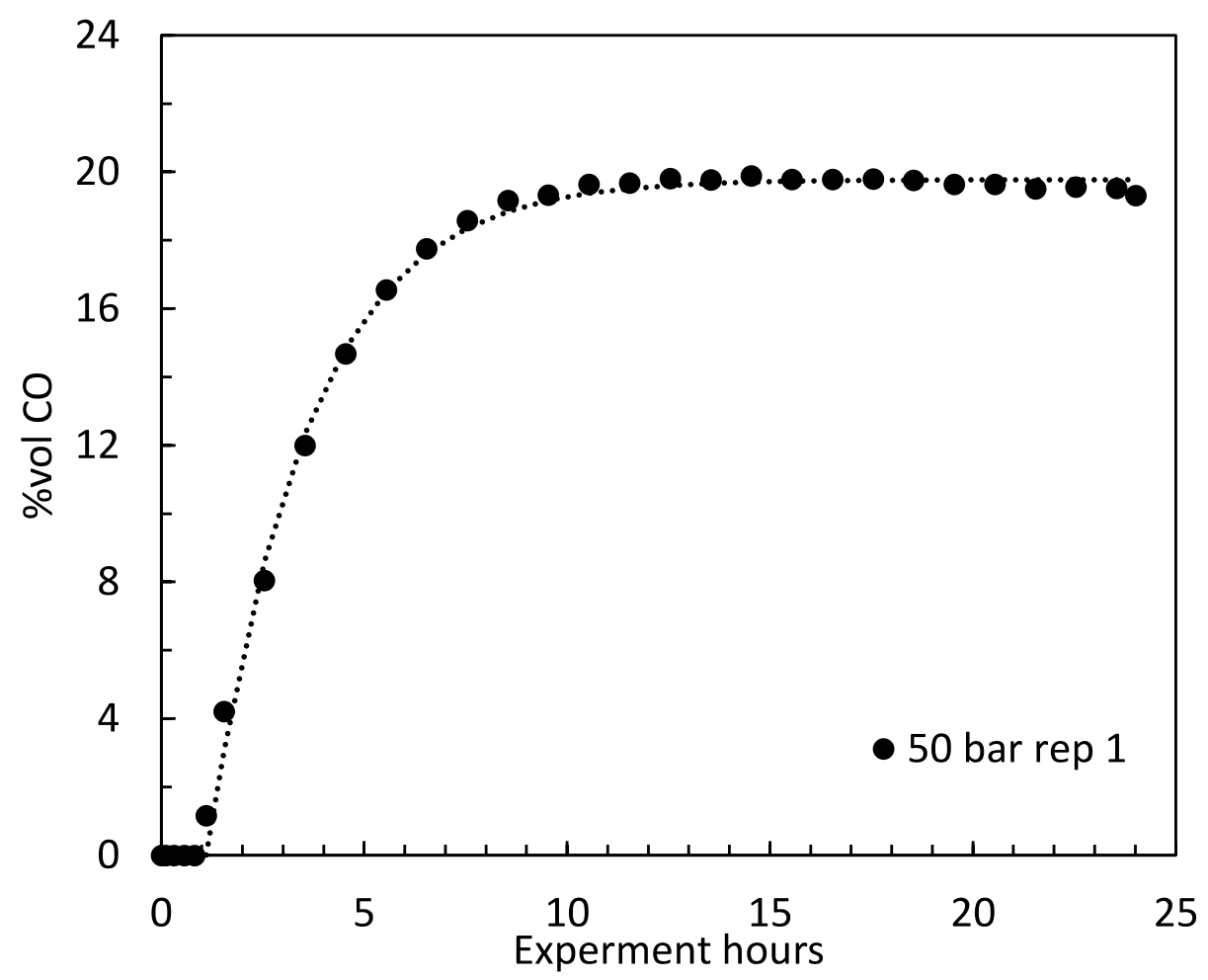


Figure 37 50 bar experiment with adjusted kinetic model

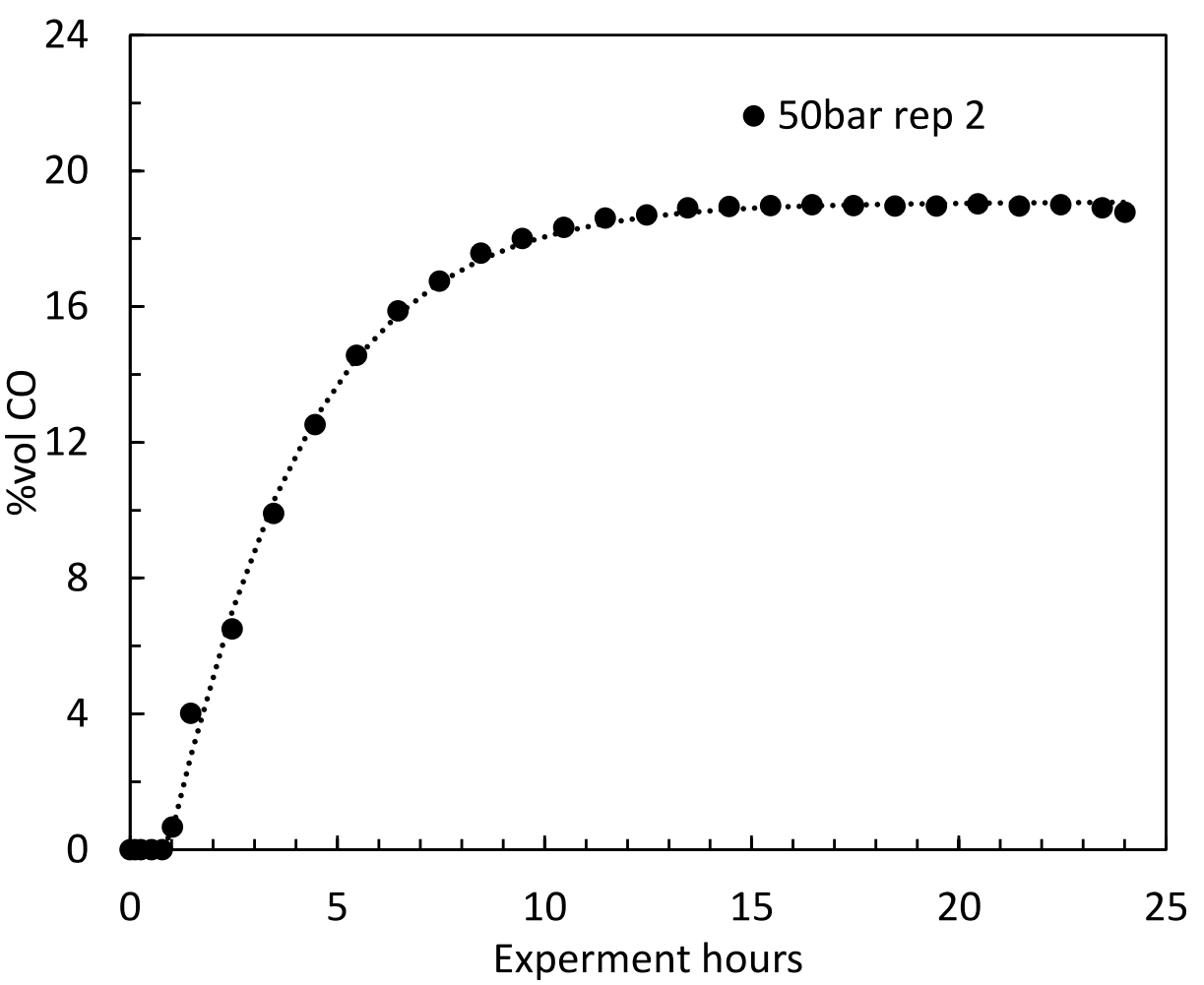


Figure 38 2nd 50 bar experiment with adjusted kinetic model

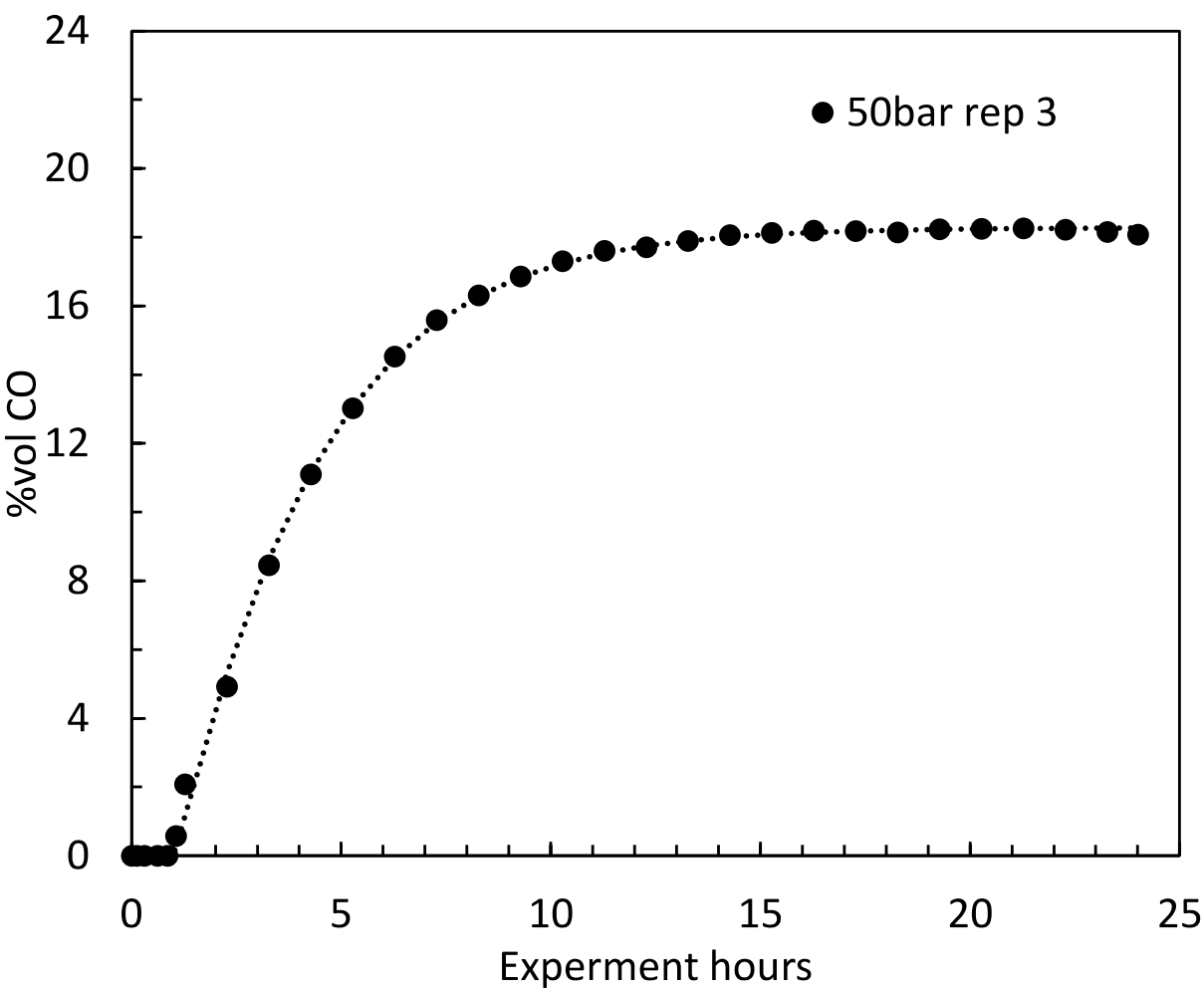


Figure 39 3rd 50 bar experiment with adjusted kinetic model

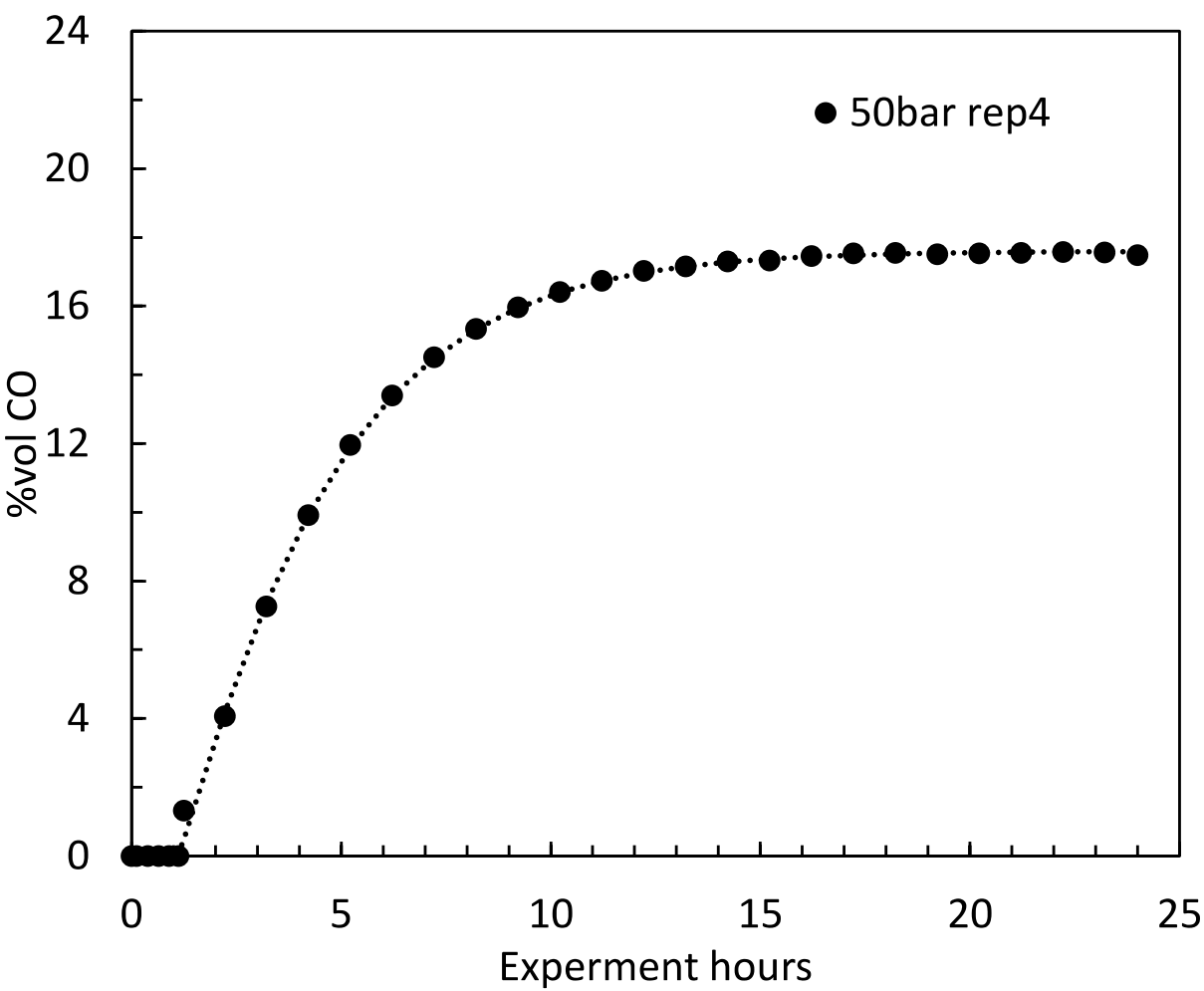


Figure 40 4th 50 bar experiment with adjusted kinetic model

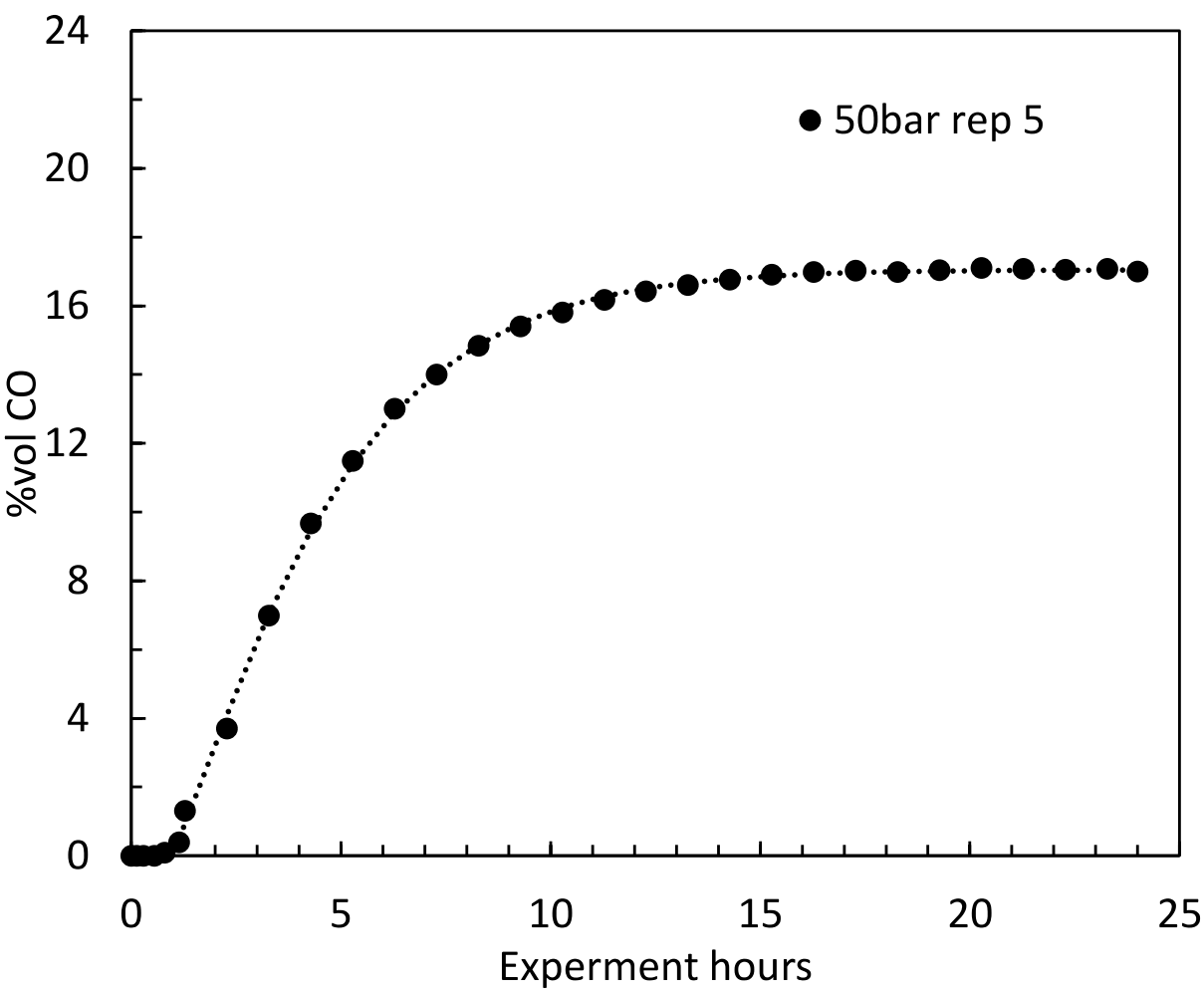


Figure 41 5th 50 bar experiment with adjusted kinetic model

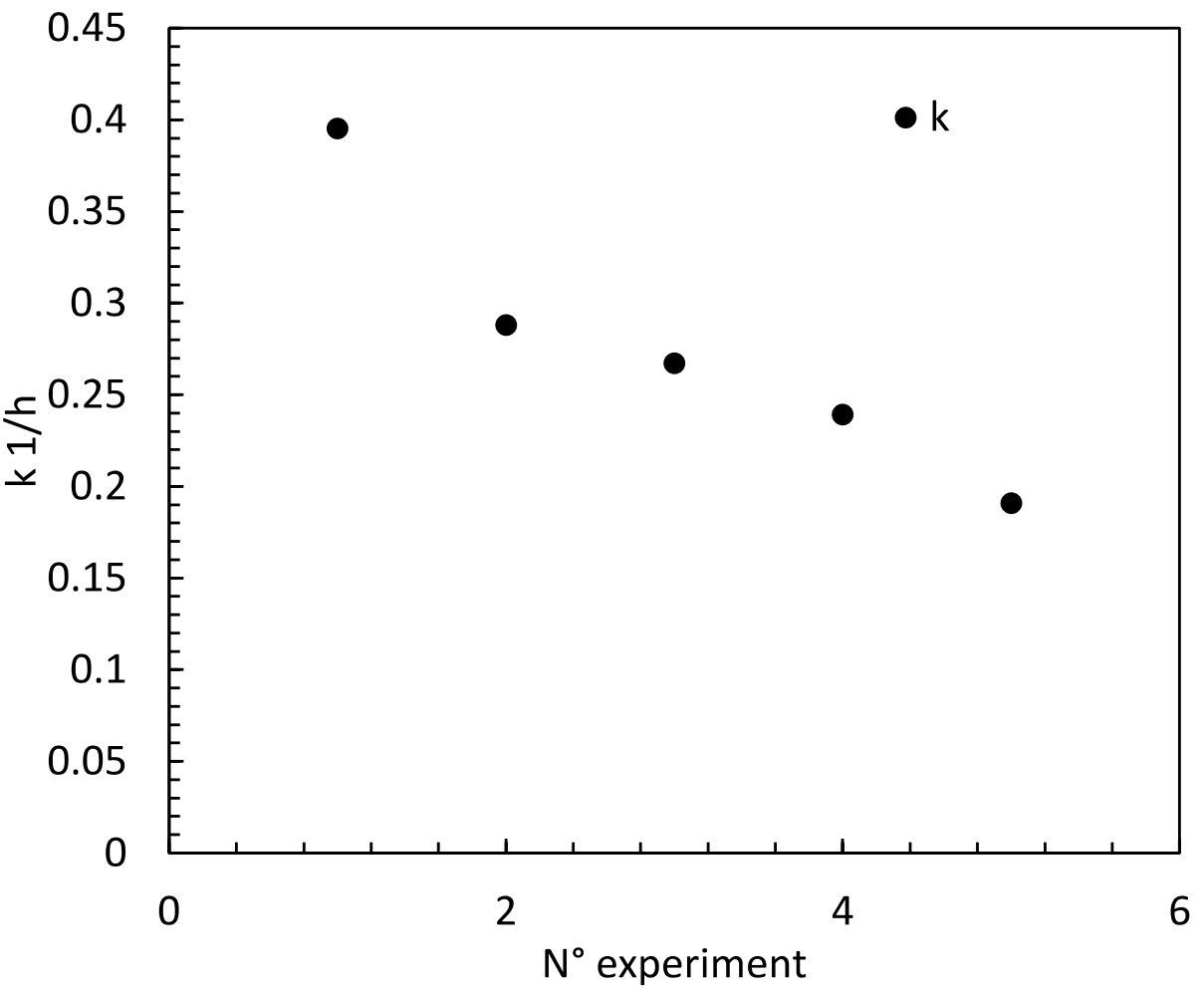


Figure 42 Change in the kinetic value of the reaction.

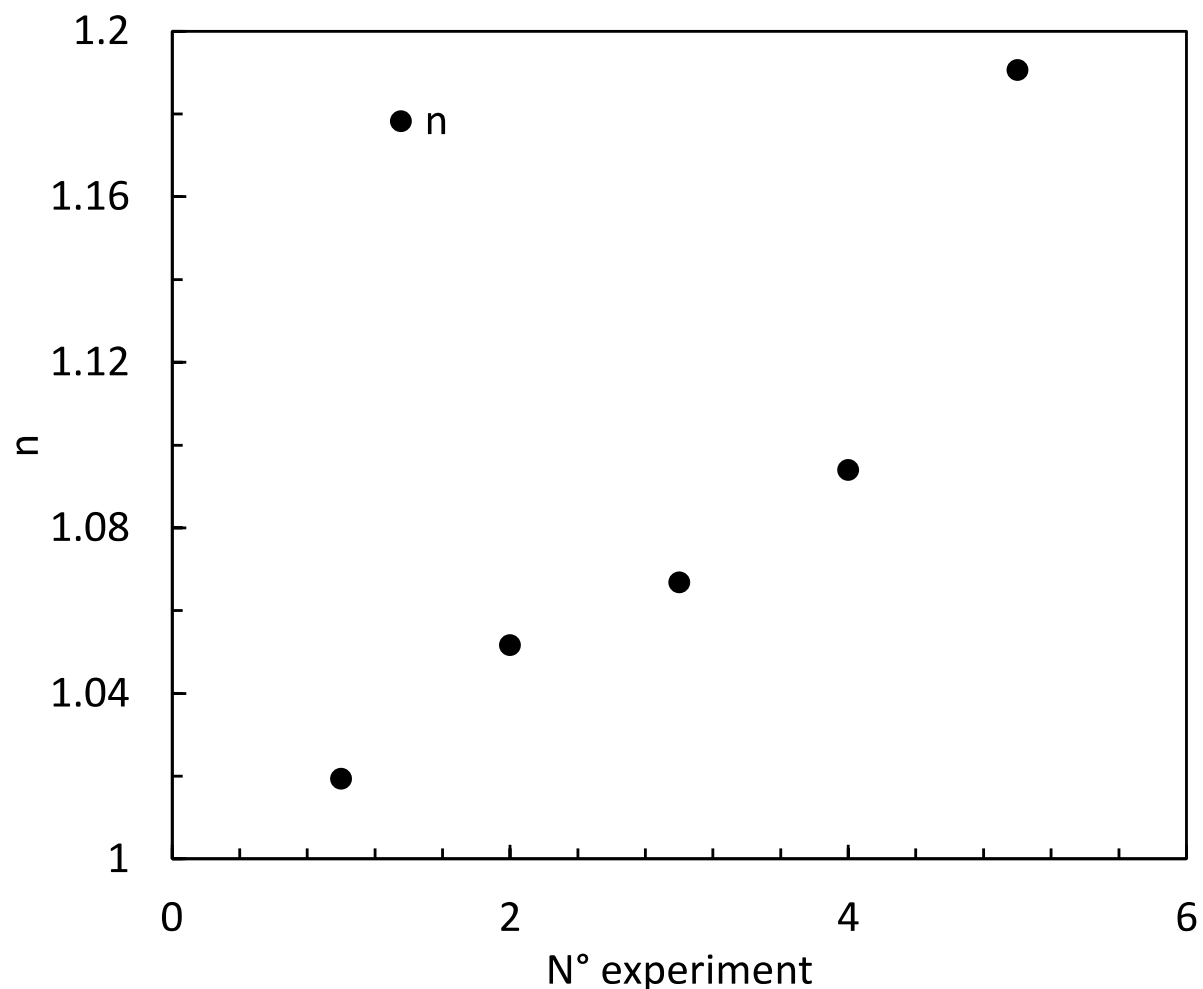


Figure 43 Change in the n factor of the reaction.

It is possible to visualize that, first, that the model adjusts practically perfect to the reaction, making it possible to conclude that, although this is a very rough approach to what the real reaction kinetics and modeling is, still is useful to describe and analyze the reaction. Secondly, the kinetic constant (Figure 42) of the overall reaction is consistently decreasing with each cycle of the reaction, this meaning that the reaction is getting constantly slower or, in other words, being diminished by the cycles, also it doesn't seem like the decrease in this factor is decelerating, therefore it is not possible to guarantee that there is a settling point where the catalyst would stop degrading.

Lastly, if the n factor (Figure 43) is analyzed is possible to say that it is increasing exponentially, this naturally goes hand to hand with the fact that the reaction is getting slower, and none of them being smaller than one, it is not a diffusion problem nor is due to a diffusion layer formed on each cycle, but more likely to be due to intrinsic changes on the catalyst properties that are resulting in a worst overall reaction.

6.7.1. Model adjustment for the High T degradation series

Following the same logic and procedure, the same model form presented on equation (6.7.1), is applied to the results obtained in the high temperature degradation series on 5.1.5, seeing already that the model does adjust, in any practical terms, perfectly to the reaction, each model adjustment figure will not be reported to avoid redundancies,

but rather the comparison between each obtained k and n values, to observe how they progress along the hours of experiment and how do they compare to a regular cyclic operation such as the one presented in the catalyst degradation series in 5.1.3.

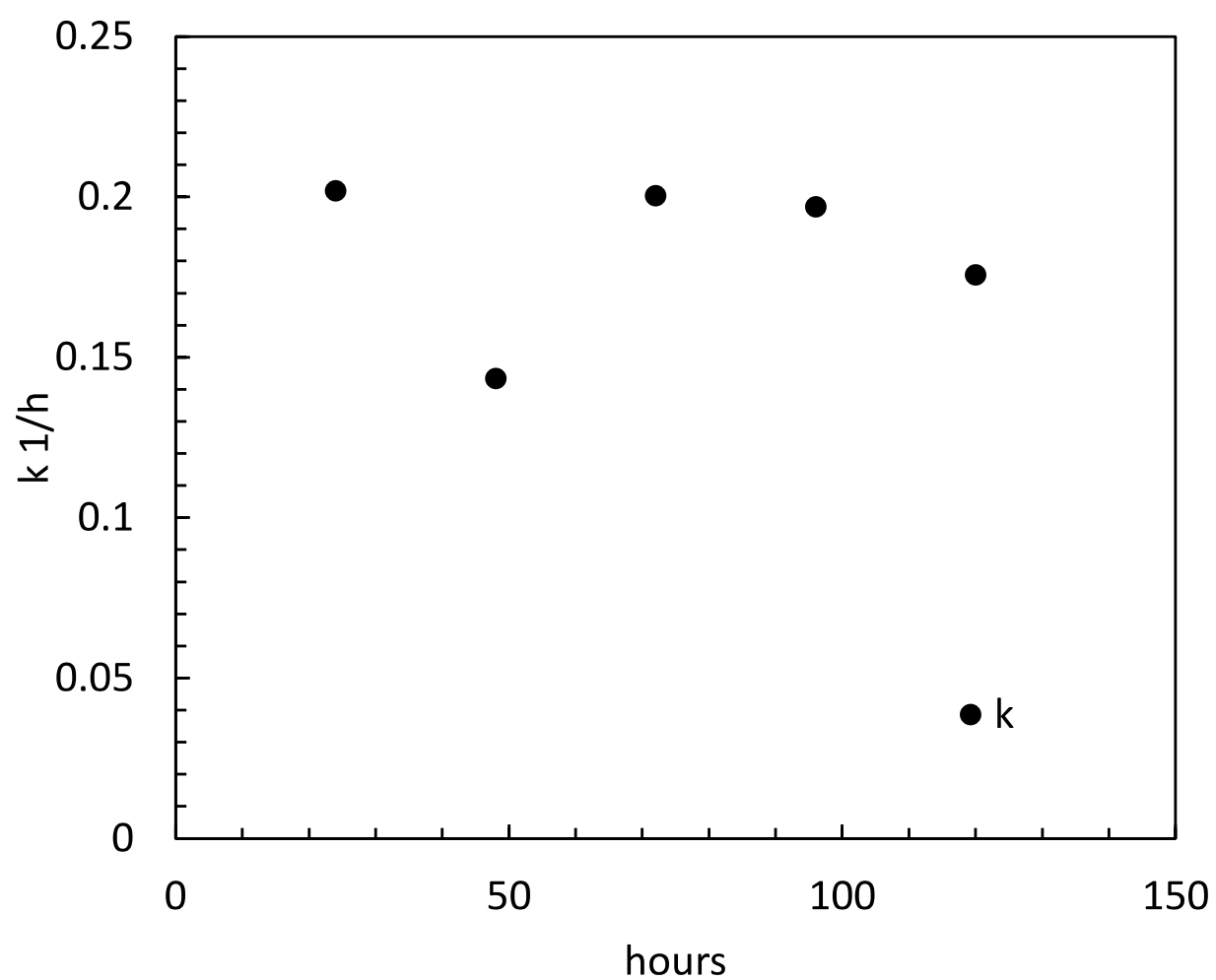


Figure 44 Change in the kinetic value of the reaction.

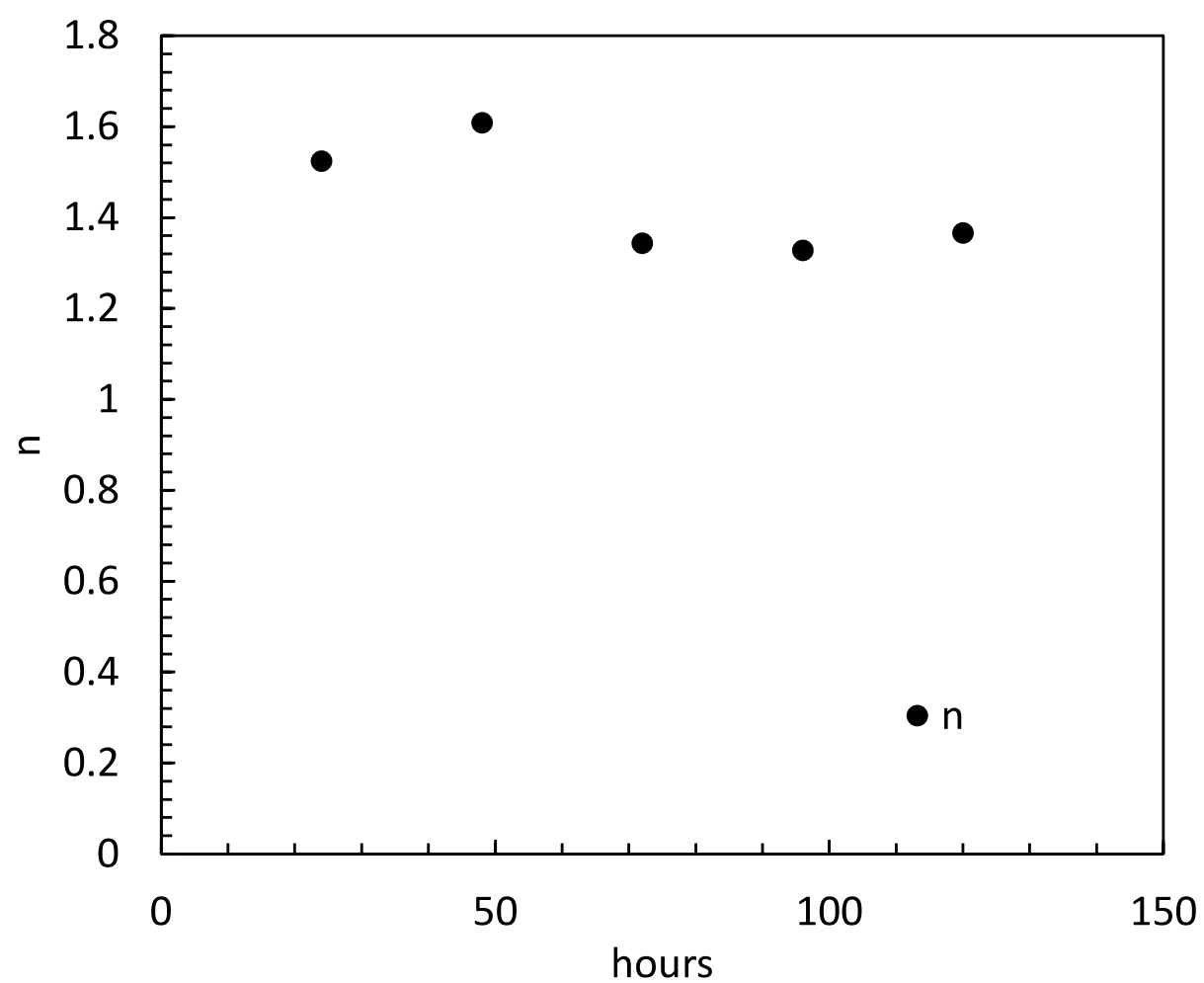


Figure 45 Change in the n factor of the reaction kinetics.

It is possible to notice that the k value (Figure 44) is substantially more consistent than the previous series, virtually observing no trend in the variation but rather oscillations surrounding an average value, yet the values are considerably smaller than the degradation in cycles, this being counteracted by the value of n (Figure 45), reaching higher values, meaning a faster approach to the plateau. It is also important to point out that, regardless of the reduction in the value of n across the experiment, this doesn't seem to follow a trending decrease, but a step decrease after the 48 hours of experiment and then staying constant across the 80 next hours.

6.7.2. Correlation of the model with the system pressure

If the different experiments summarized on 6.4 are evaluated and adjusted to the model presented on the equation (6.7.1), it is possible to evaluate the differences on the kinetics depending on the pressure of the reaction, although the model not being exact it could give valuable information to face future experiments. Again, to provide with precise and concise information, each adjusted model is going to be omitted, and only the n and k factors are to be evaluated.

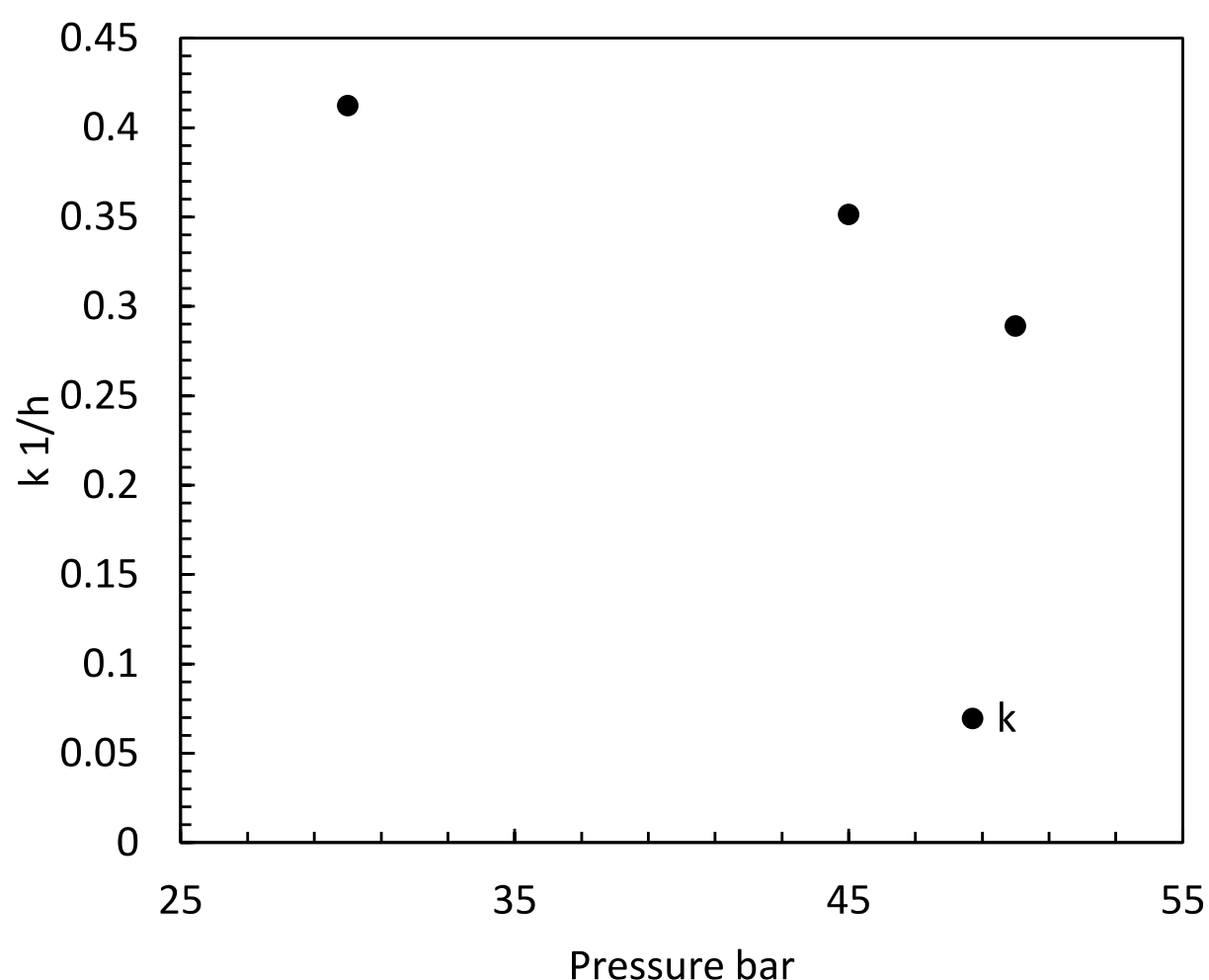


Figure 46 Kinetic value over different pressure

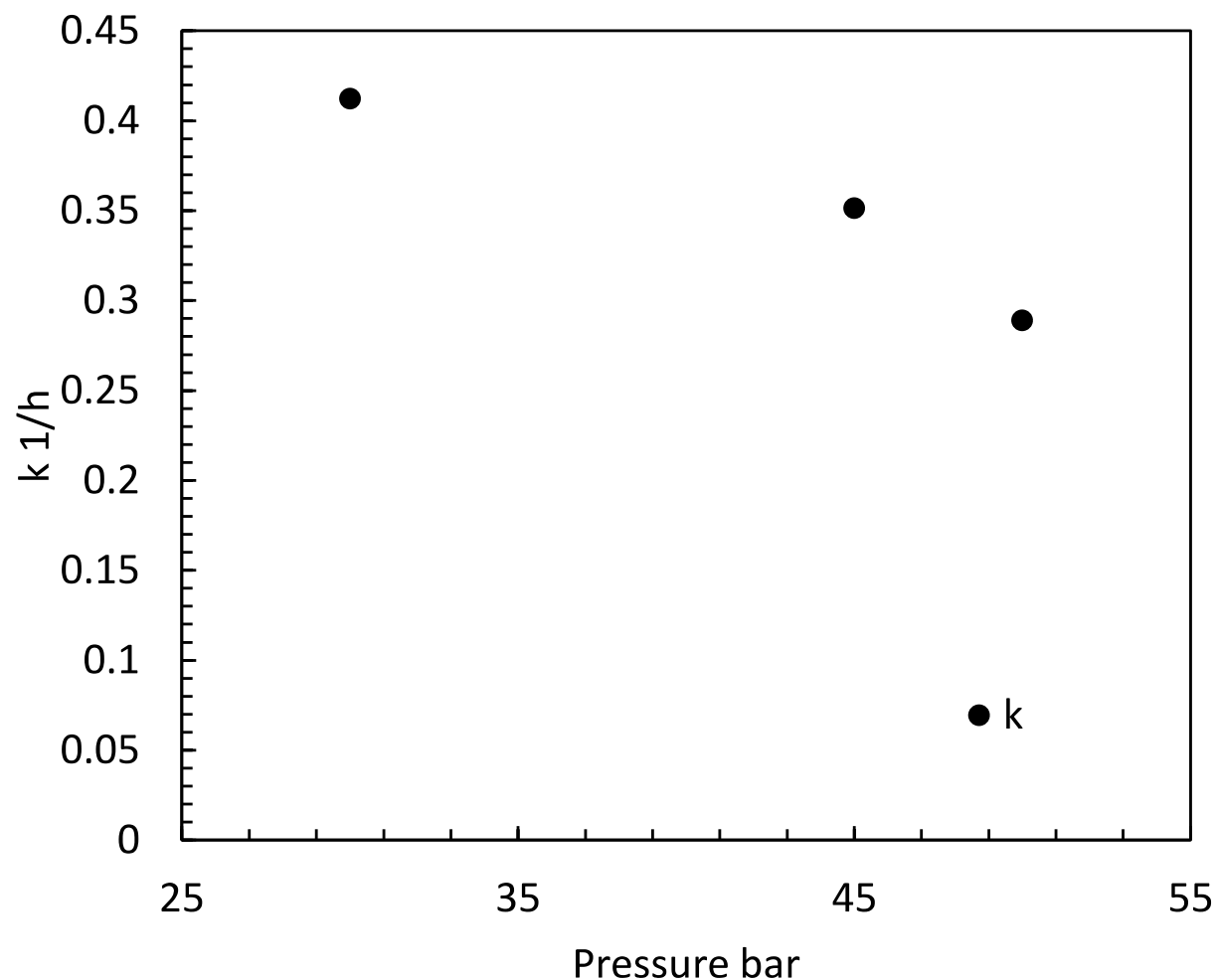


Figure 47 n factor over different pressure

While it seems counterintuitive to find that the kinetic value is decreasing with the increase in pressure (Figure 46), yet still getting better performance in every experiment assessed at 50 bar over the ones realized at 30 or 45 bar, this can be explained by the fact that, for this study, the only way of analyzing the data on real time during the experiment is quantifying the gas composition, and the main objective is to produce methanol, a liquid product, therefore is not a part of the gas phase of the reaction, although it is theorized that for the methanol production a higher rate on the reverse water shift reaction is required, the reaction of CO hydrogenation gets considerably better performance at increasing pressure, then both reactions happening at the same time in the reaction, at higher pressure it is expected to obtain a lesser peak in the monoxide composition, due to the augment in the rate of methanol generation, having both the RWGS and the CO hydrogenation competing at the same time. Concluding that the RGWS kinetics are incremented at lower pressures, but the hydrogenation kinetics are diminished by this condition, resulting in a higher plateau or CO %vol equilibrium point, but a lesser methanol rate of production.

Regarding the n factor (Figure 47), it is possible to see that neither of the obtained results are under 1.00, thus the reaction is not being determined or controlled by a diffusion situation.

6.7.3. Correlation of the model with the catalyst composition

Based now in the proposed model over the results obtained in 5.1.1 and 6.1, the reaction kinetics are evaluated to see the relation with the copper loading in the catalyst. The adjustments can be found in Annex, while in this part of the report only the obtained final factors and constants are to be evaluated.

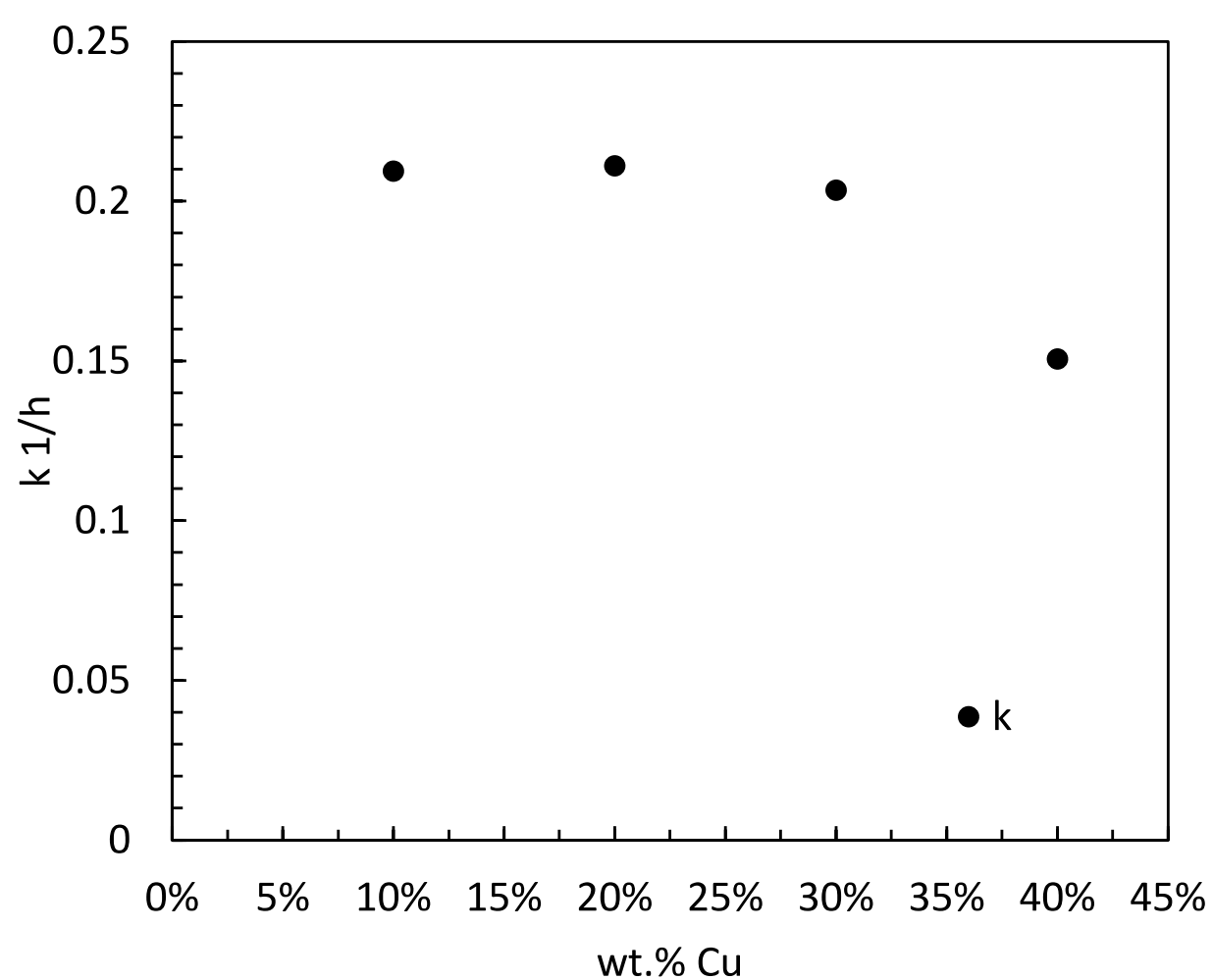


Figure 48 Kinetic value over the catalyst composition

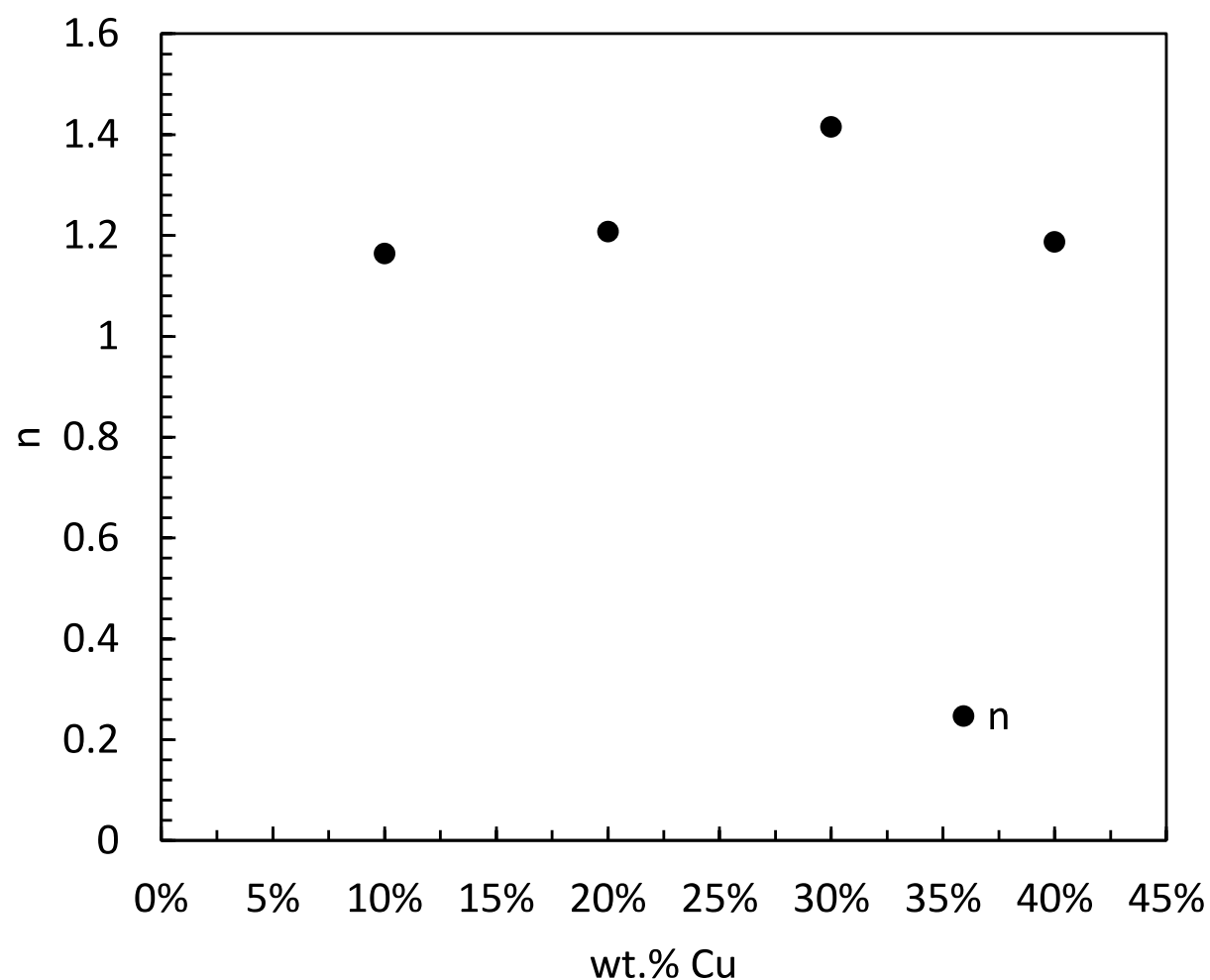


Figure 49 n factor over the catalyst composition

It is possible to observe that there is a slight increase in the value of the n factor (Figure 49) towards 30% copper content, decreasing again when approaching 40%, with a very clear decrease when the kinetic constant is analyzed (Figure 48), observing an rapid decrease when increasing the copper content over 30%, this may be explained by clustering effect, since the catalyst is prepared only by impregnation methods, therefore the catalyst is mainly MgO impregnated or “covered” with Cu particles, thus if the amount of copper increases over a certain limit, the active areas and the interface of MgO and Cu starts disappearing due to the copper clustering the magnesium in the core of the particles.

6.7.4. Correlation of the model with the circulating load

The circulating load within the system affects heavily to the process, both in theory and observed in the results obtained in 5.1.2 and 6.2, altering the flow field inside the reactor, the interface interaction between the solid and the gas phase, among several other factors, thus it is expected to have some correlation with the proposed kinetic model presented in Figure 50 and Figure 51.

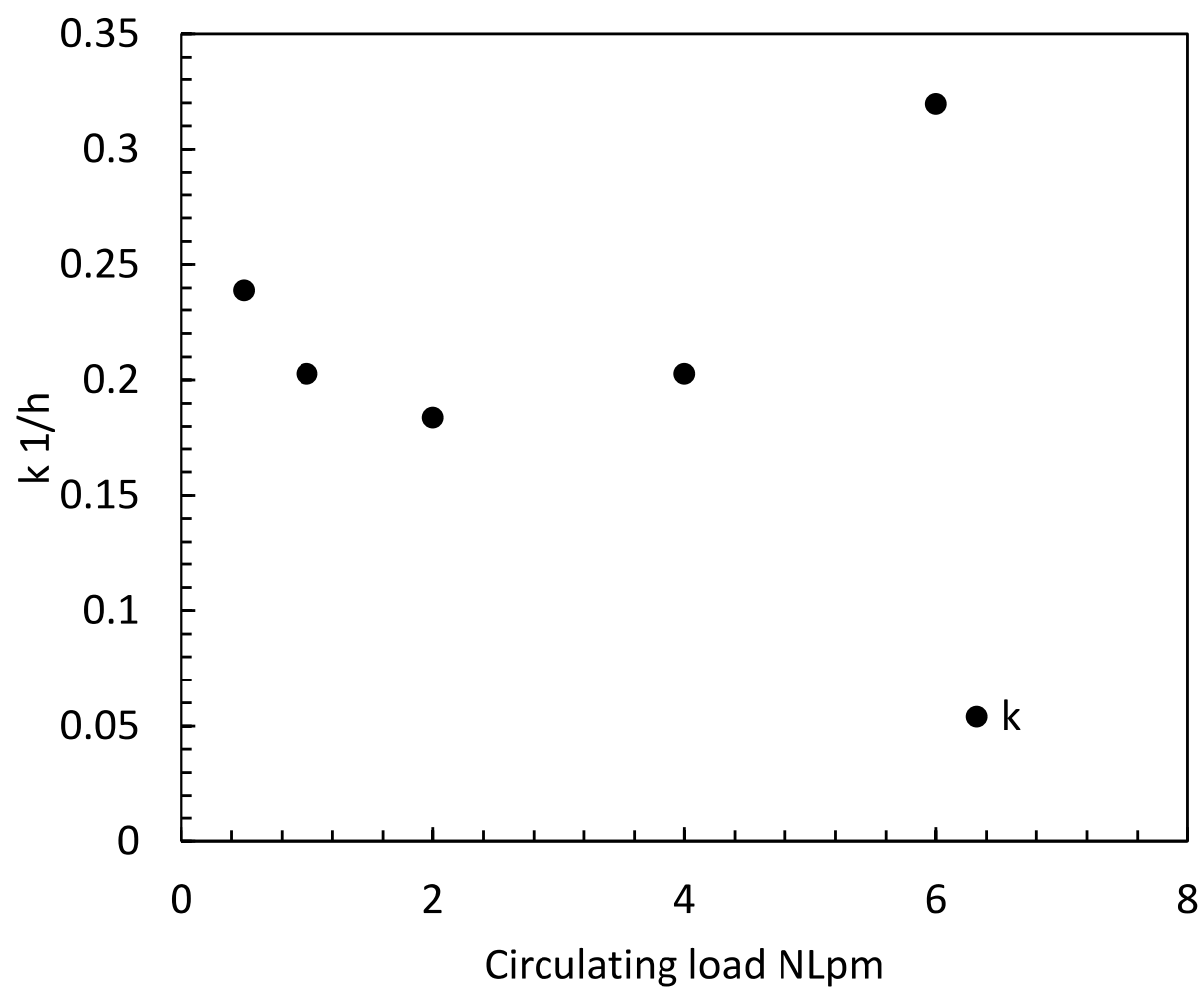


Figure 50 Kinetic value over the circulating load of the system

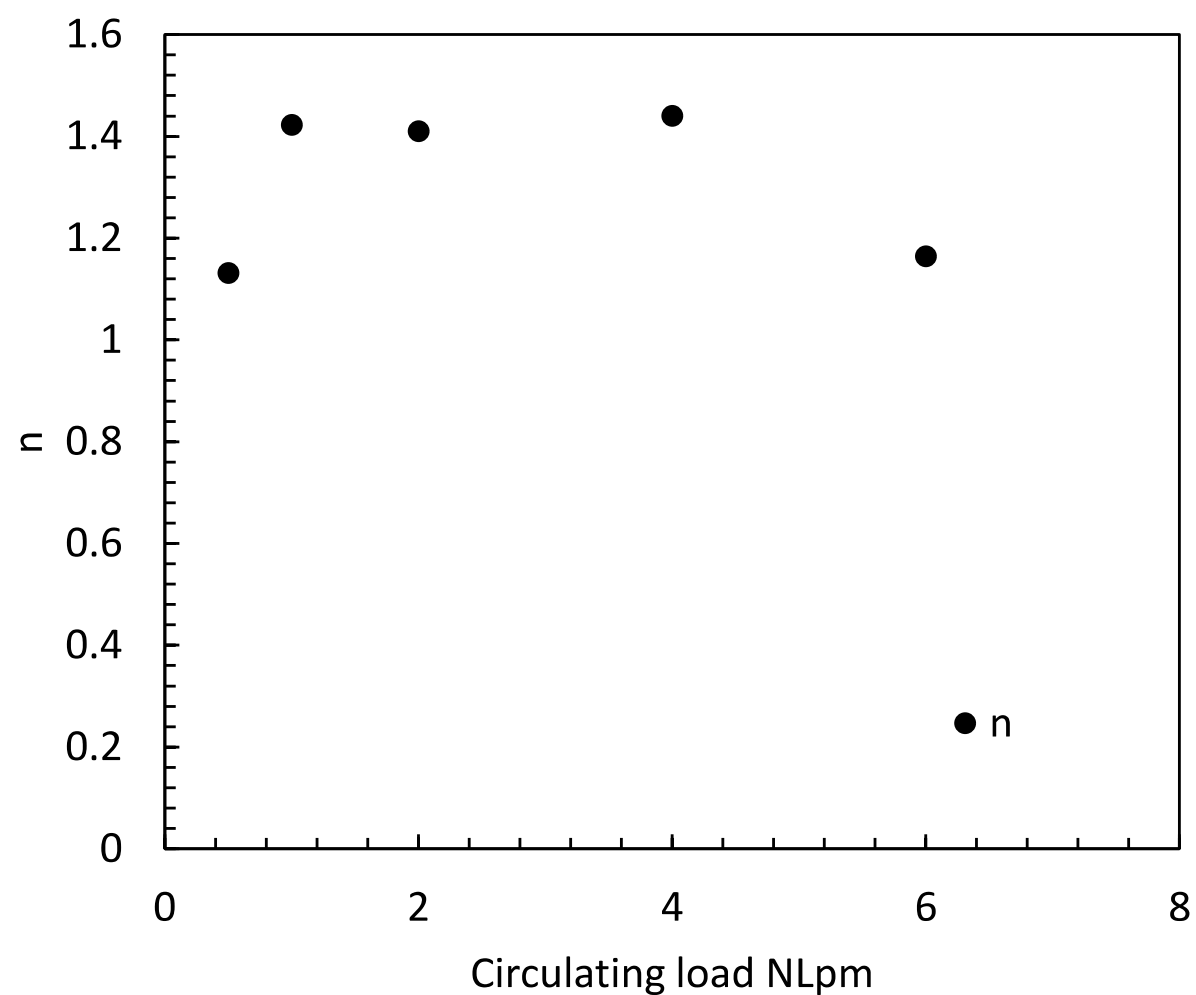


Figure 51 n factor over the circulating load of the system

It is noticeable how the kinetic factor has a substantial effect over the circulating load of the system, behaving practically perfectly as a quadratic relation, reaching the minimum around 3 NLpm, this and again as explained in the section 6.7.2, is contradictory when compared to the actual methanol production rate obtained in section 6.2, due to

the RWGS being more favorable than the CO hydrogenation, when incremented over certain limit, the rate of production of CO dominates over the rate of production of methanol, due to it having slower kinetics, then obtaining a higher CO equilibrium value but a lower methanol production rate in time. On the other hand, when comparing the effect over the n value, it doesn't seem to have any effect over the circulating load.

7. Process scale-up and Design proposal

To do a process scale up from the obtained data, is important to take into consideration the fact that the concluded experiments and the proposed process is a holistic view for a lab-scale process that still needs to be proven on a pilot-lab, pilot plant and later a real-life scenario, thus the system proposed is not for an industrial plant but rather a pilot-scale model in order to assess the different needs of this reaction, evaluating more options for the reactor such as pneumatic transport reactor or fluidized bed.

7.1. Pilot-Process design proposal

The main goal from this study is to integrate a catalytic reactor to the direct siderite reduction system to close the gap from the already 60% CO₂ emissions reduction to a higher percentage, this by capturing the exhaust gases from the direct reduction, and using them as the feed gas, on which the carbon oxides will be converted to methanol, breaching the gap from that remaining 40%. The net reduction in emissions from this process will be considered as shown in equations 9.1.1 and 9.1.2:

$$\%CO_{2\text{ siderite}} + (100\% - \%CO_{2\text{ siderite}}) \cdot \gamma_{MeOH} = \%CO_{2\text{ Net Reduction}} \quad (9.1.1)$$

Applying the numbers that are already known:

$$60\% + (40\% \cdot \gamma_{MeOH}) = \%CO_{2\text{ Net Reduction}} \quad (9.1.2)$$

Obtaining that the net emissions reduction is directly given by the yield of conversion from carbon oxides to methanol. Having that in mind, the design shown in Figure 52 is proposed. For the design of the process is considered an initial feed of only hydrogen, but with the possibility of feeding nitrogen in case is needed for measurements or for neutralizing purposes.

The main direct reduction reactor is changed from a packed bed to a continuous screw reactor (Archimedes screw), to make a countercurrent continuous reactor, since in a real-life scenario is unlikely, especially in the mining industry, the use of batch or any kind of non-continuous process.

The design of the pilot includes an energy integration system, where the gases coming out of the direct reduction, at temperatures in the order of 700°C are utilized to heat up the catalytic reactor, to later pass through the condenser where the water is separated,

to then a compression for the injection into the catalyst reactor, later heat exchanger to finally get to the condensation vessel where the product is obtained, and the non-condensable stream is recycled into the reactor. Is important to point out that there is a purge included in the case of inert gases accumulating in the system.

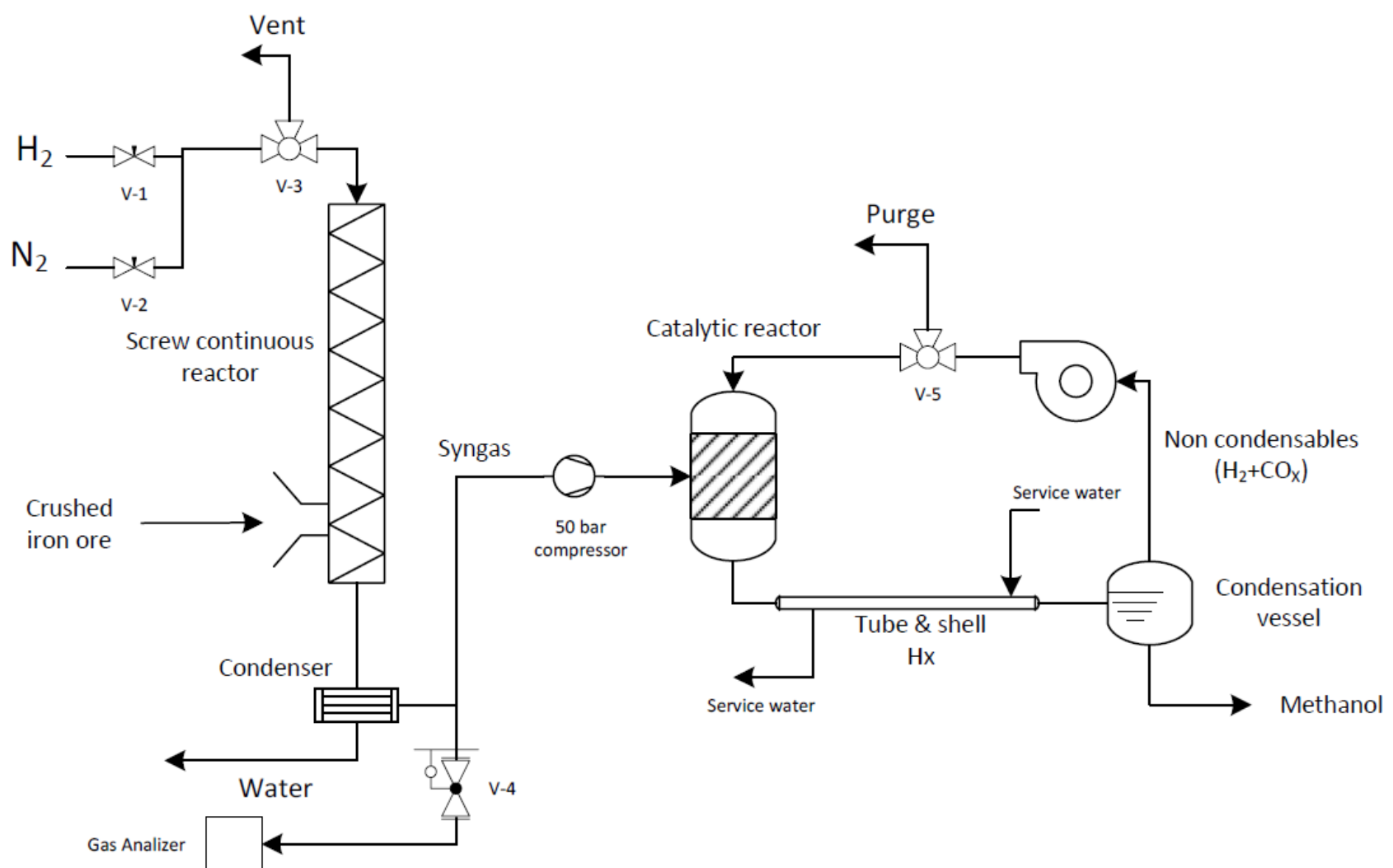


Figure 52 Process design proposal for an integrated direct reduction-hydrogenation reactor system

Due to the nature and the conditions tested on the laboratory scale reactor, it is proposed that a monolithic tubular reactor is evaluated, based on previous works done by Hurtado et al. [42] show the improvements of the usage of this reactor when compared to the traditional catalytic packed beds, this in combination with the high yields obtained with the use of MgO , it is arguable to expect promising results by combining this two technologies. Yet, to design and dimension a monolithic honeycomb reactor, substantial amounts of work and data that are not available would be required, escaping the main objectives of this specific study which are the technical evaluation of the feasibility of the process in a lab-scale. Consequently, for simplification and simulation processes, the reactor proposed is a traditional Gibbs reactor.

7.2. Reactor proposal

In previous studies realized by Hurtado et al [43] the usage of a catalytic tubular reactor was evaluated for the conversion of CO_2 to methanol using the $\text{Cu/ZnO/Al}_2\text{O}_3$ (CP-488) commercial catalyst, which although being reported to have underwhelming performance on high CO_2 environments, with the usage of the monolithic honeycomb-type tubular reactor, shown in Figure 53, efficiencies of up to 25% of CO_2 conversion. The main advantage of providing a much more homogeneous residence time distribution while also making the residence time effective interfacial contact time between the reactive gases and the catalyst. On the other hand, the evaluated reactor for this experiment, was composed of a traditional reaction vessel, having the catalyst forming a film on the bottom of it, resulting in most of the reactor being dead, unused space, not providing anything to the reaction but to increase the residence time, without the implication of this meaning a longer interfacial contact time.

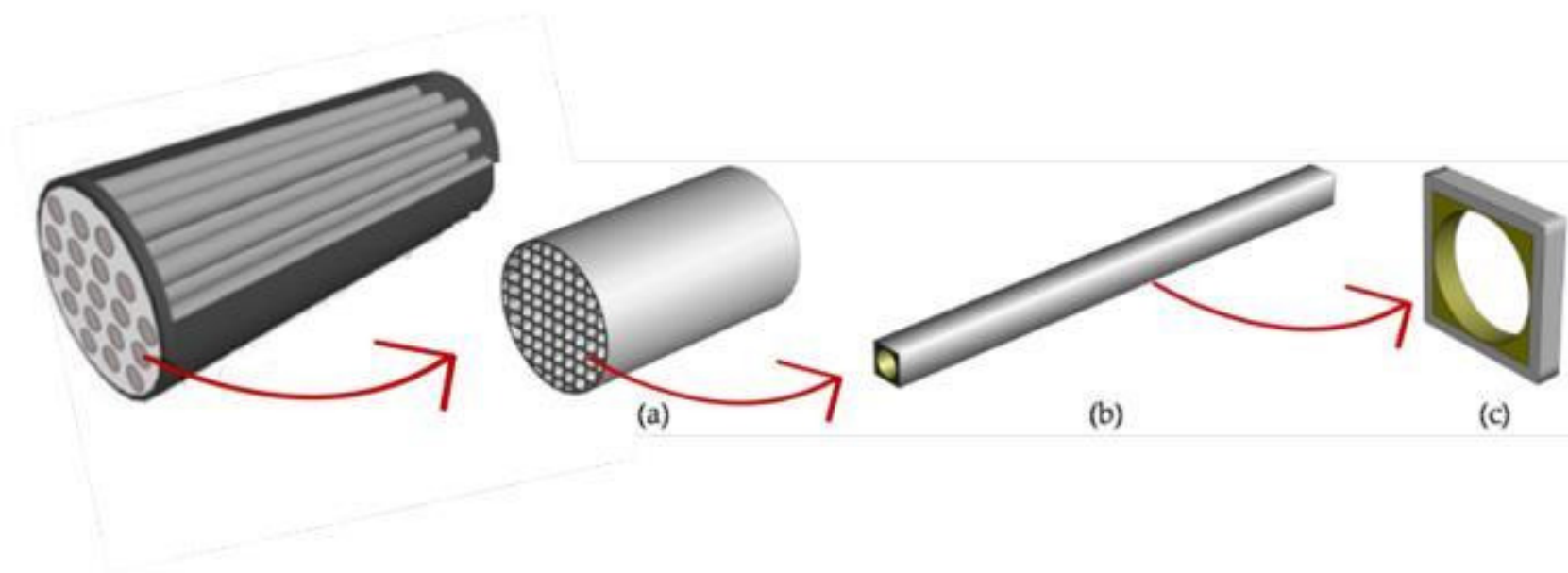


Figure 53 Diagram of a generic honeycomb-type tubular reactor [43]

With the combination of this work, implementing the more effective Cu/MgO catalyst assessed on this study, it is expected that much more promising results can be obtained, yet because of both economic and timetable limitations, it is not possible to evaluate such system, but rather leave it as a proposal for future projects.

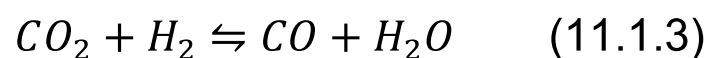
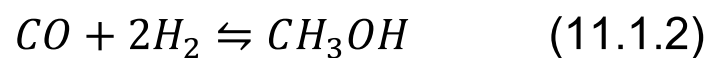
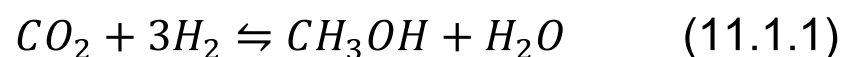
8. Process simulation (ASPEN)

This chapter is focused on the simulation of the process of CO_2 hydrogenation using the chemical process engineering software Aspen HYSYS, to use as a reference point for comparison with the estimated production values presented on Process scale-up and Design.

8.1. Simulation parameters

For the simulation the fluid model utilized is the Peng-Robinson to determine the state variables, due to its robustness as a model within non-ideal conditions such as the ones presented in the CO_2 hydrogenation, with high temperatures, non-ideal pressure conditions, non-simple molecules, and reactions.

The reaction set considered is the equilibrium reaction set composed of all the water shift, reverse water shift and carbon hydrogenation reactions mentioned on 3 Theoretical background, Figure 6. The equilibrium reaction used are listed on (11.1.1) to (11.1.3)



The equilibrium parameter for the mentioned reactions, are obtained from the Aspen Properties library and are dependent on the fluid conditions, thus intrinsically linked to the thermodynamic fluid model. The model is only analyzed in steady state conditions.

The feed gas conditions are replicated from 7 Process scale-up and Design, considering 3 kg/h of a 75% hydrogen 25% CO_2 mixture, and the circulating load determined by the software's calculations.

8.2. Simulation

The simulation is made using a Gibbs reactor, with a preheating unit, and a later total condenser, the product is separated on a product tank, where the non-condensable products are repressurized and recycled to the reactor. A short explanation of every unit operation required for the simulation is presented as follows.

MIX-100: A mixing unit where the fresh feed, presented as “FRESH” is mixed with the recycle stream, presented as “RECYCLE”, obtaining the “COLD FEED” stream, which is later heated to the desired temperature on the E-100 heat exchanger.

GBR-100: The main reactor for the process, where the equilibrium reactions occur, in it the three equilibrium reactions happen at a temperature of 350°C and 50bar of pressure, obtaining a “PRODUCT” stream which contains all the resulting products of the reaction, later cooled down to 25°C on the E-101 unit operation, there is also a “LIQUID” stream that is required on this type of reactor, but it doesn't have any influence in the process, since every single component in GBR-100 is gaseous or vapor.

V-100: A separation vessel, analogue to the product vessel utilized on the lab-scale reactor, where on the bottom a final product is obtained on the stream “MeOH/WATER”, and all the rest of the non-condensable products leave the reactor by the top on the “NON-CONDENSABLE” stream.

K-100: Due to pressure losses during all the mentioned processes, a compressor is needed to repressurize the stream again to the initial 50bar, forcing the flow within the system, obtaining the “RECYCLE 50BAR” stream.

RCY-1: A virtual recycle unit, utilized for iteration and calculation purposes, that makes the software system know that the resulting “RECYCLE 50BAR” stream is going inside the system again as the “RECYCLE” stream.

The resulting simulation is presented on Figure 54.

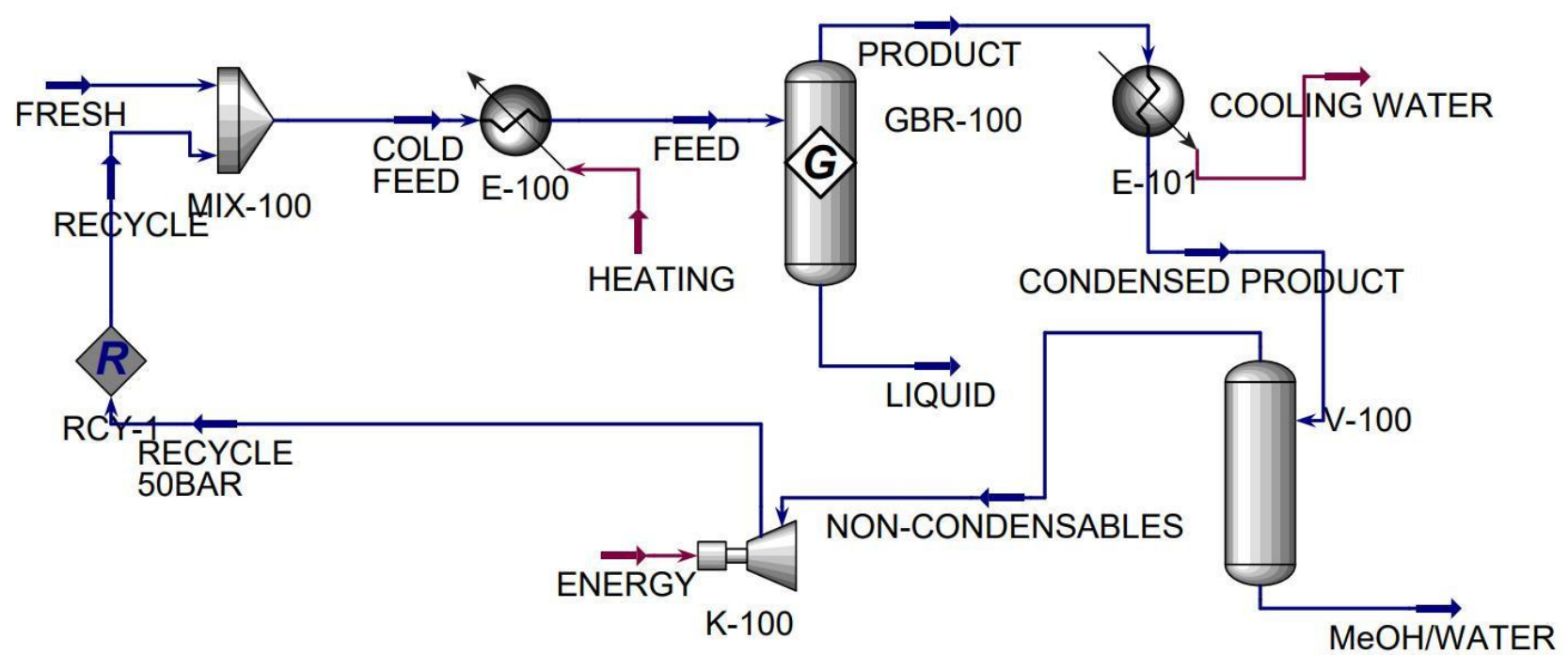


Figure 54 Process general diagram generated on Aspen HYSYS

The specification of the relevant streams is summarized on Table 9.

Table 9 Relevant stream flows and composition

	<i>Unit</i>	FRESH	FEED	PRODUCT	NON-CONDENSABLES	MeOH WATER	RECYCLE
Mass Flow	kg/h	3.00	113.56	113.56	109.86	3.00	110.56
Molar Flow	Kmol/h	0.24	11.21	11.04	10.90	0.14	10.97
H ₂ Fraction		0.75	0.71	0.70	0.71	0.00	0.71
MeOH Fraction		0	0.00	0.01	0.00	0.58	0.00
CO Fraction		0	0.25	0.25	0.25	0.00	0.25
CO ₂ Fraction		0.25	0.04	0.04	0.04	0.01	0.04
H ₂ O Fraction		0	0.00	0.01	0.00	0.42	0.00

8.3. Simulation analysis

It can be observed that there is an hourly production of methanol equivalent to 2.6 kg/h, or 1874 kg/month of pure methanol, number which is smaller than the obtained in the process scale up, nevertheless it is important to point out two main factors that might affect the production of this simulation. Primarily, the reaction is simulated as an equilibrium Gibbs system, while in real life the proposed process is a heterogeneous catalyzed reaction. The Aspen software does include the catalytic reaction option, but due to the unknown kinetics and details of the CO_2 hydrogenation, it was preferred to avoid this type of simulation and use a regular equilibrium just as an approach. Secondly, it is believed that maybe the 350°C may not be the optimal operation point, why it was made a sensitivity analysis of the process when changing the temperature of the feed and thus the temperature of the reactor and reaction, which are dependent on this variable.

A sensitivity analysis was carried out by varying the temperature of the FEED stream, analyzing the effects on the MeOH/WATER stream, which represents the final product of this process. The temperature was modified from 50°C to 600°C at different steps to compare the results and conclude regarding the amount of net product and MeOH composition in the stream. The obtained results are presented on Figure 55 and Figure 56.

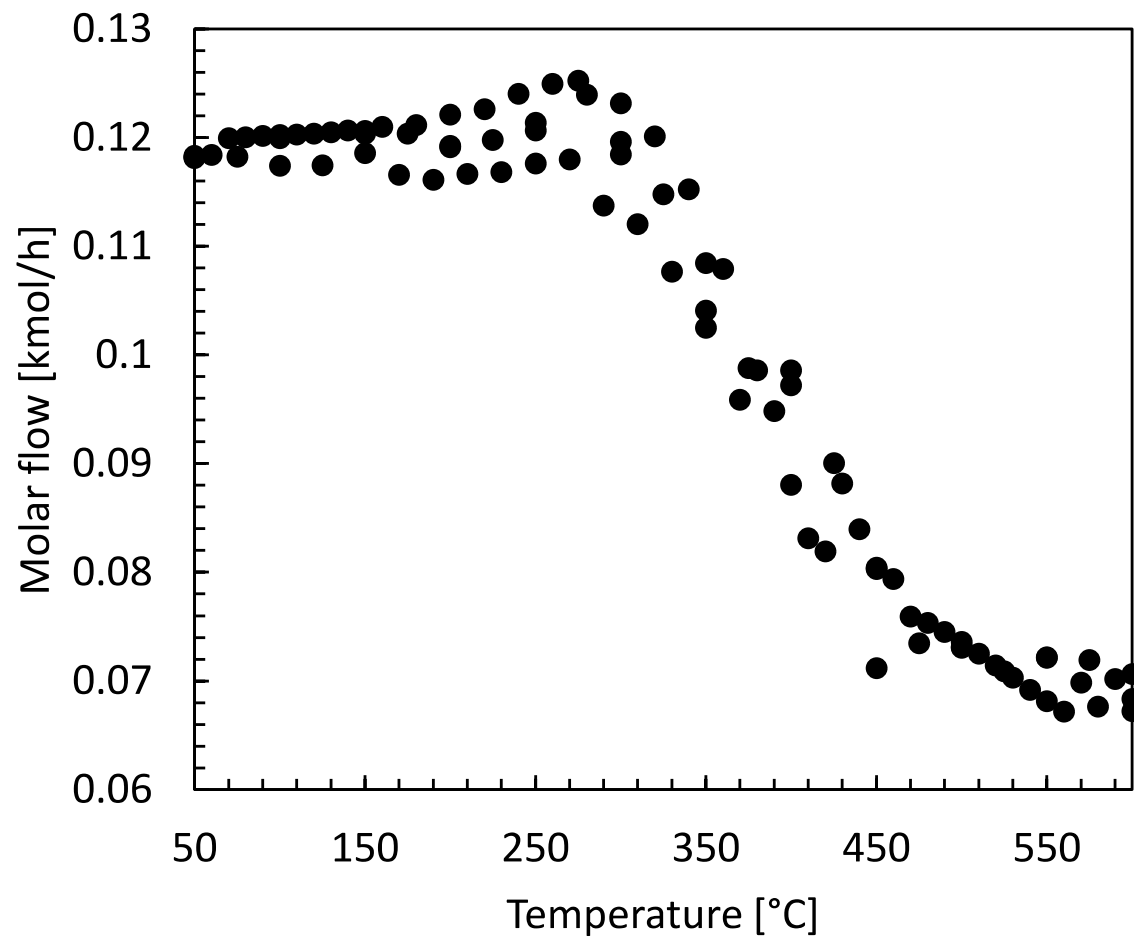


Figure 55 Effect of reaction temperature on total product outflow

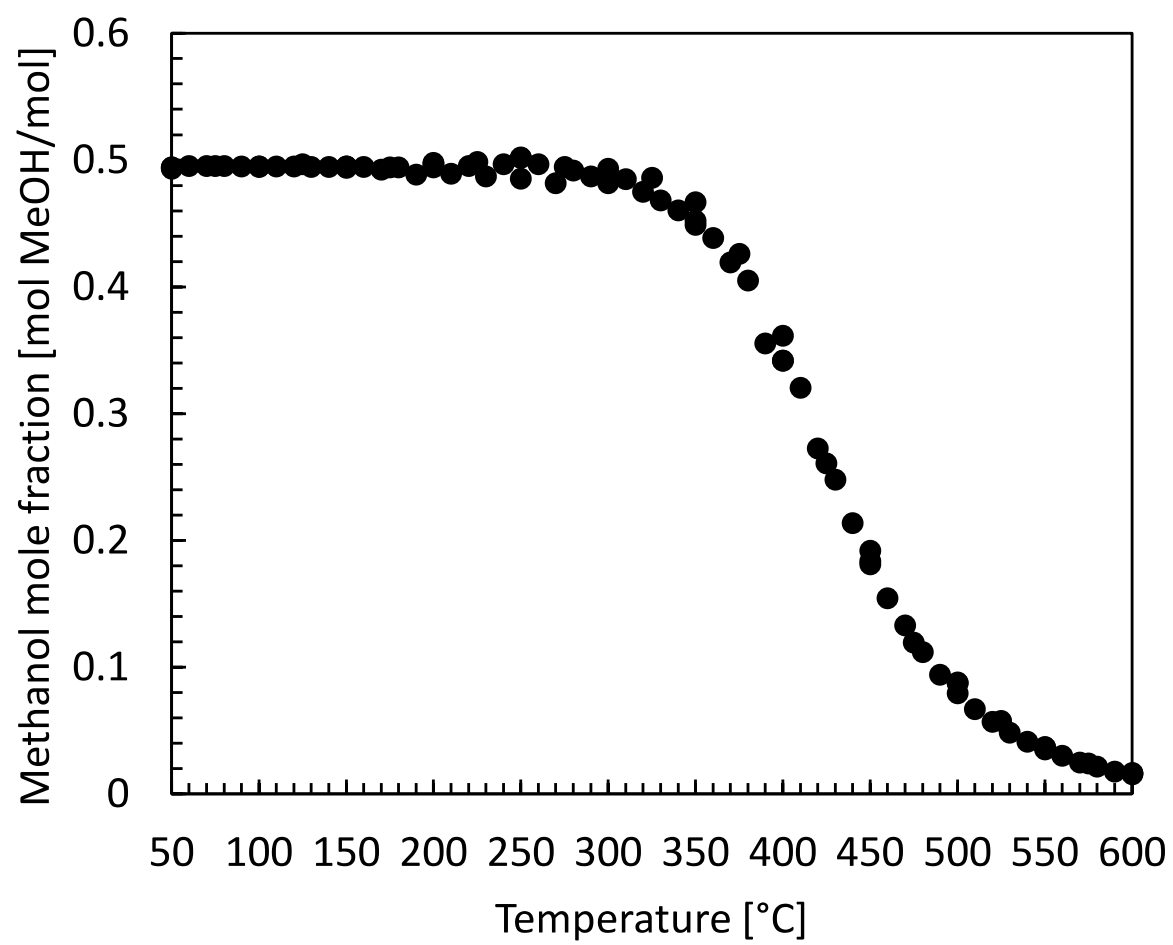


Figure 56 Temperature reaction effect on the product composition

To remove uncertainty regarding the robustness of the sensitivity analysis, the iterations were repeated three times, with different step sizes and slightly different starting and ending points, whereas if the solution to the iterations was considerably different from one to another, then it could mean that the system was not solved but the maxi-

mum number of iterations was reached. It can be observed both in Figure 55 and Figure 56, that the results don't vary considerably, obtaining points oscillating around an average for similar values of temperature.

It can be observed that there is a breakthrough after 300°C, where both the overall production and the composition of such a product is severely affected, this explains why the production is significantly lower compared to the process scale up proposed.

In any case, both for the process scale up, and the simulation to continue studying the effect of the methanol, the reaction kinetics and pilot testing the proposed system, since the mere attempt of doing an industrial scale process straight from a lab-scale reactor implicates errors in the order of 30-50% if not even more.

9. Conclusion and recommendations

Having finalized the study, the main conclusions for this report are

- The hydrogenation of the exhaust waste stream produced on the siderite's direct reduction process into methanol is technically possible as it was demonstrated to be achievable using a single copper-magnesia catalyst achieving yields over 75% of conversion from the worst-case scenario where the feed is composed only by hydrogen and CO₂.
- Hydrogenation is in practical terms, feasible as the utilized CuMgO catalyst is reusable and recyclable as a slug former in the mining industry, allowing a continuous process and not generating unnecessary waste.
- The catalyst is overly sensitive to gross temperature oscillation thus for maximum performance of it, the operation must be done at a constant temperature. The best conditions from the experiments realized are at 20wt.% copper loading, a high recirculation rate, 1300°C of magnesia calcination temperature and operating the system at a pressure of 50 bar.
- There is no initial apparent need to add an extra component to the catalyst composition, since the CuMgO can reach high efficiencies and yield of conversion without the need for further complication in the process, although it may be possible to improve even further the benchmark if the process of synthesis changes or there is another component added to it.
- With the combined effects of the siderite's direct reduction and the proposed hydrogenation of the waste stream, a reduction in carbon emissions of 90% is achieved when compared to a traditional siderite mining process with the use of a conventional coke blast furnace and a sintering plant. Nevertheless, it is important to point out the fact that this is considering that the hydrogen utilized corresponds to green hydrogen, if not, then the emissions may be higher due to the carbon footprint associated with the hydrogen production.
- MgO based catalysts present a promising alternative to traditional alumina catalysts for syngas conversion, increasing the spectrum of existing possibilities for CO₂ revalorization, and opening the possibility of combining the positive results of this catalyst with other state of the art technologies.

9.1. Recommendations

Considering the experiments done, the results observed and the potential of this vein of investigation, the following recommendations are made to further development of both the reaction mining and the catalytic hydrogenation technologies and processes.

- Considering the plant design and the augment in the operation costs and reactor size when scaling up, it might be more convenient to consider the option of utilizing parallel smaller reactors to treat the feedstock.
- Due to the physical and material limitations of the performed experimentation, there was no option of fixing the catalyst in place rather than just placing it inside the reactor. It would be recommended that for further experiments, the catalyst is fixed in place, allowing the use of much higher recirculation rates, or the utilization of a film based monolithic tubular reactor to achieve effective interface contact times in a much more controlled volume, probably achieving much higher results.
- Furthermore, for material limitations, it couldn't be tested a procedure maintaining constant pressure within the system, although the reproducibility was achieved and there was practically no catalyst degradation, the efficiency and the yield may can stay even higher if the system stays constantly at the same conditions.
- The methodology used for preparing the CuMgO catalyst was by impregnation, explaining why over certain limit, the amount of copper in it starts affecting negatively to the yield, this could be changed by evaluating different methods of catalyst synthesis such as coprecipitation, where the possibility of clustering is almost non-existent.
- It is recommended that the evaluation of adding other components in small quantities to the catalyst such as zinc, titanium, or aluminum, if they are in small weight percentages, they should make more difficult the process of recycling and might be tailored better to the process.
- Finally, this experiment evaluated only the possibility with an iron ore starting point, but in theory it might be possible to do it in other metallic ores, such as copper where the mineral product, being copper may function as the catalyst and reducing both processes to only one.

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11. Annex

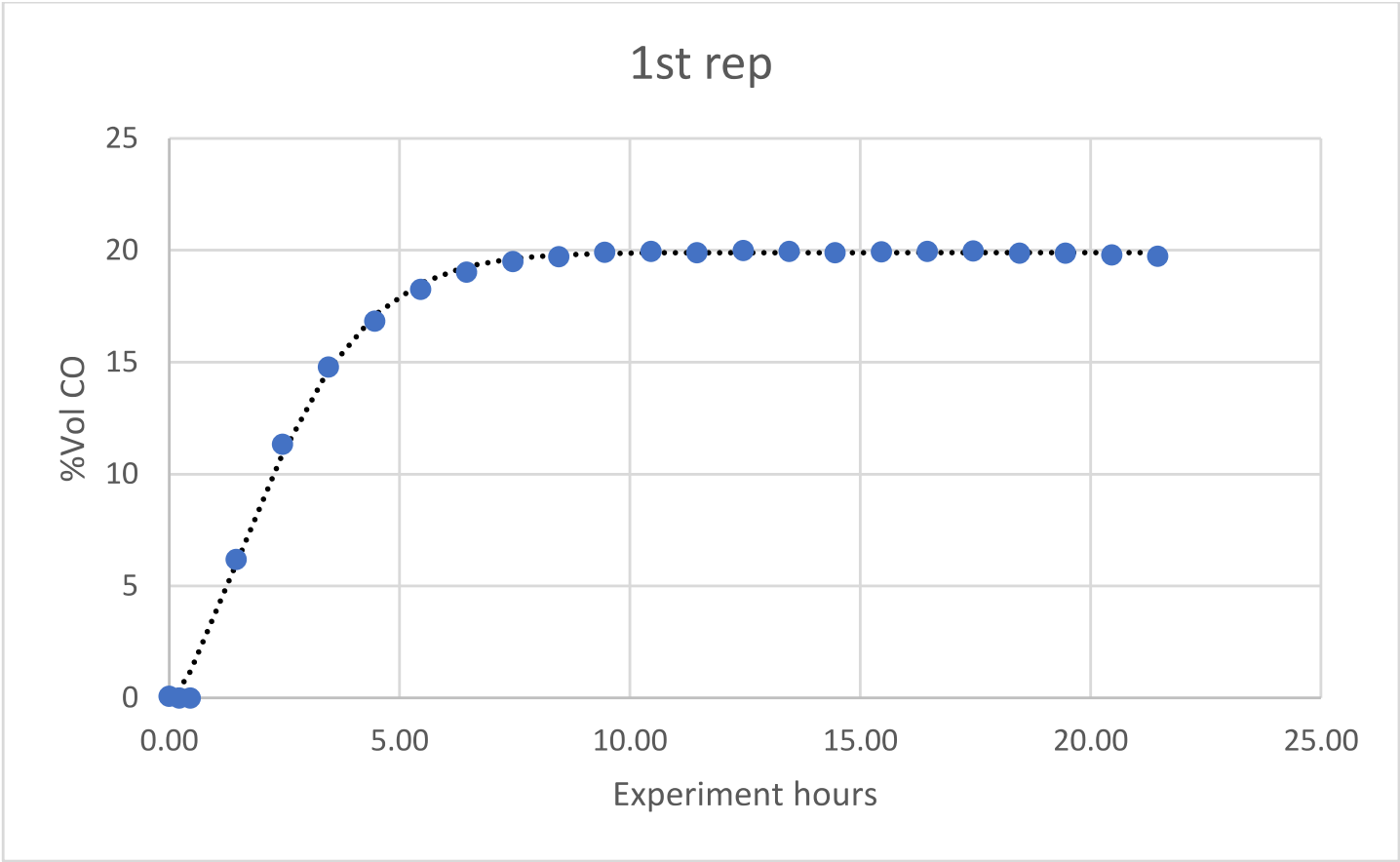


Figure 57 High temperature operation model rep 1

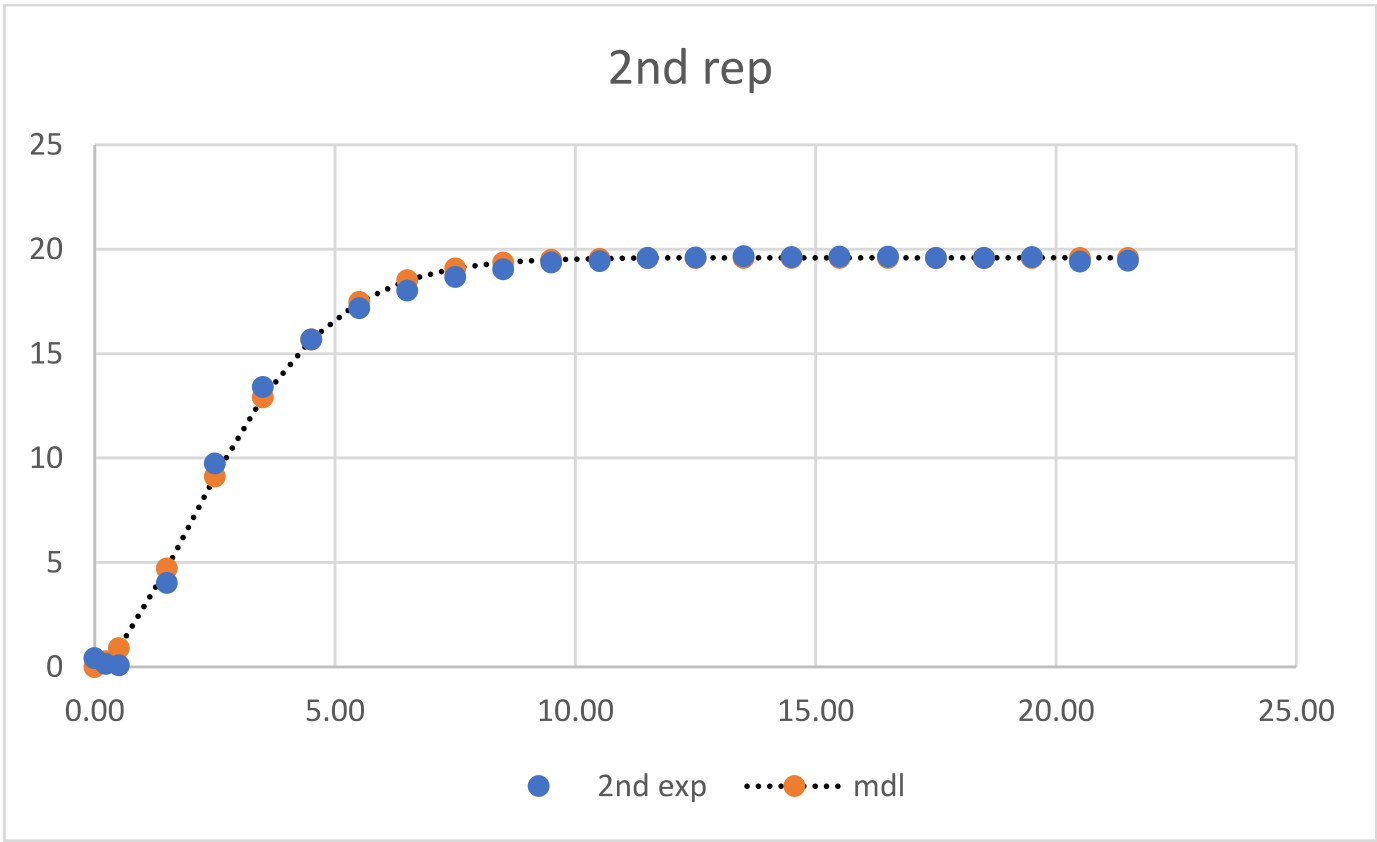


Figure 58 High temperature operation model rep 2

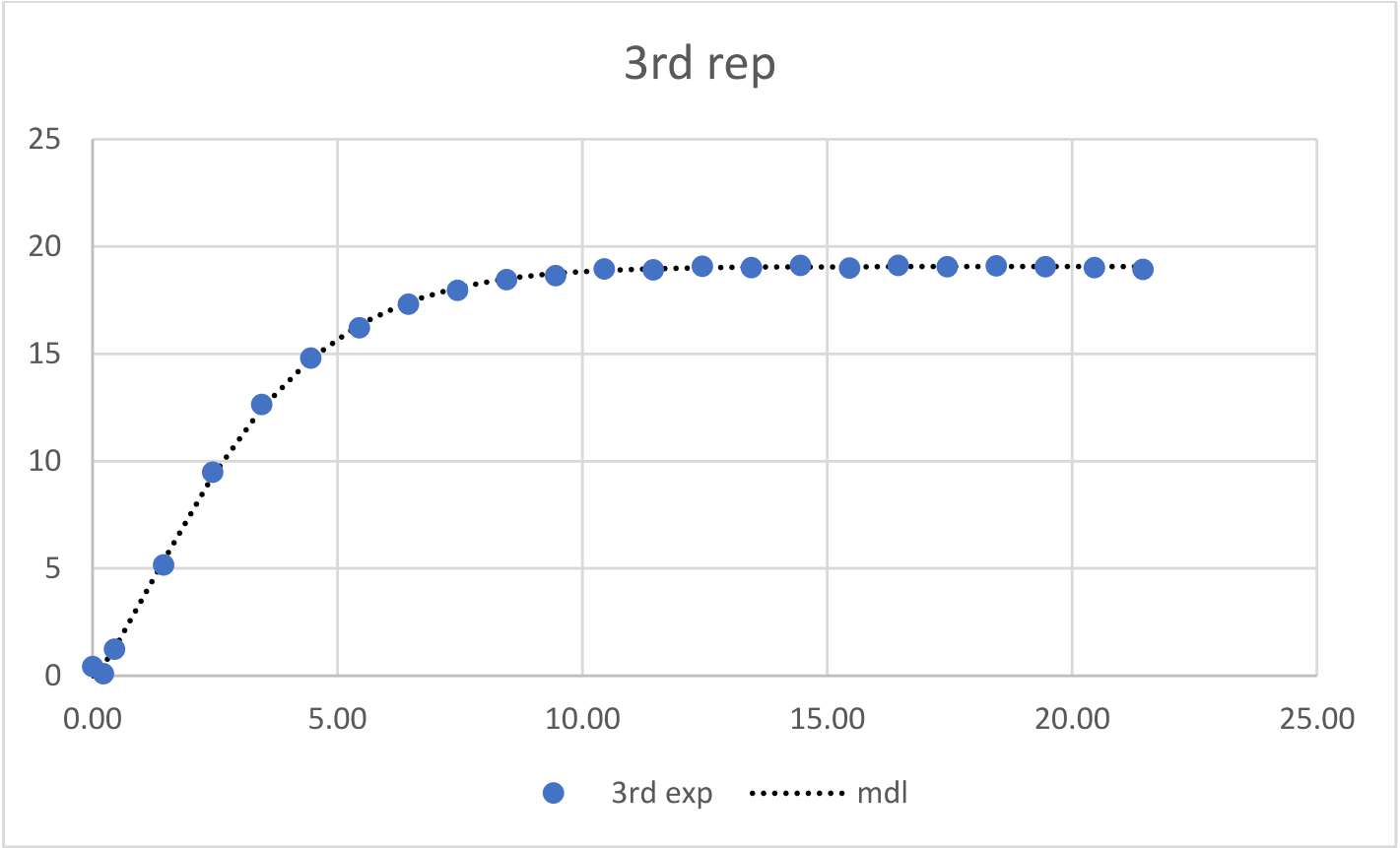


Figure 59 High temperature operation model rep 3

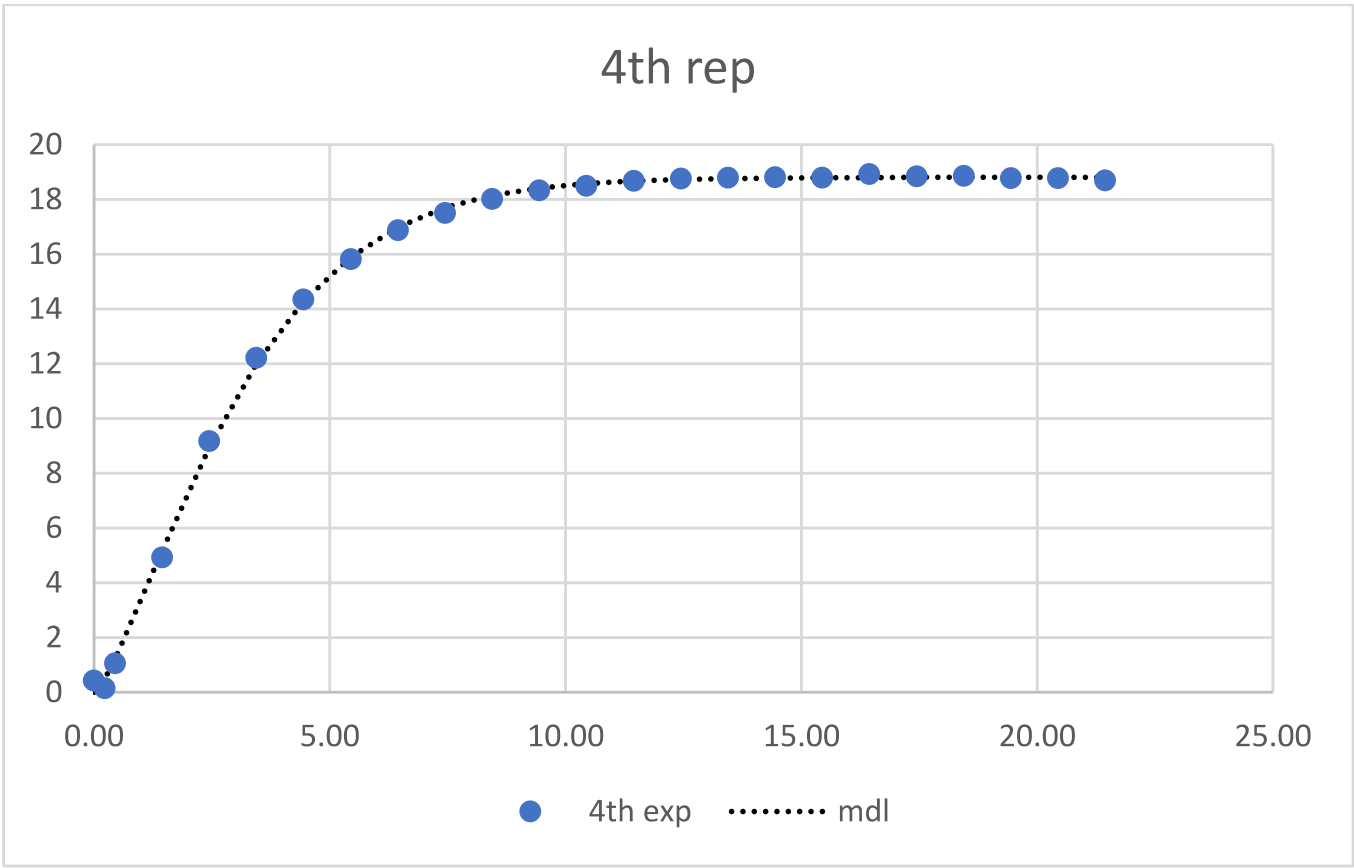


Figure 60 High temperature operation model rep 4

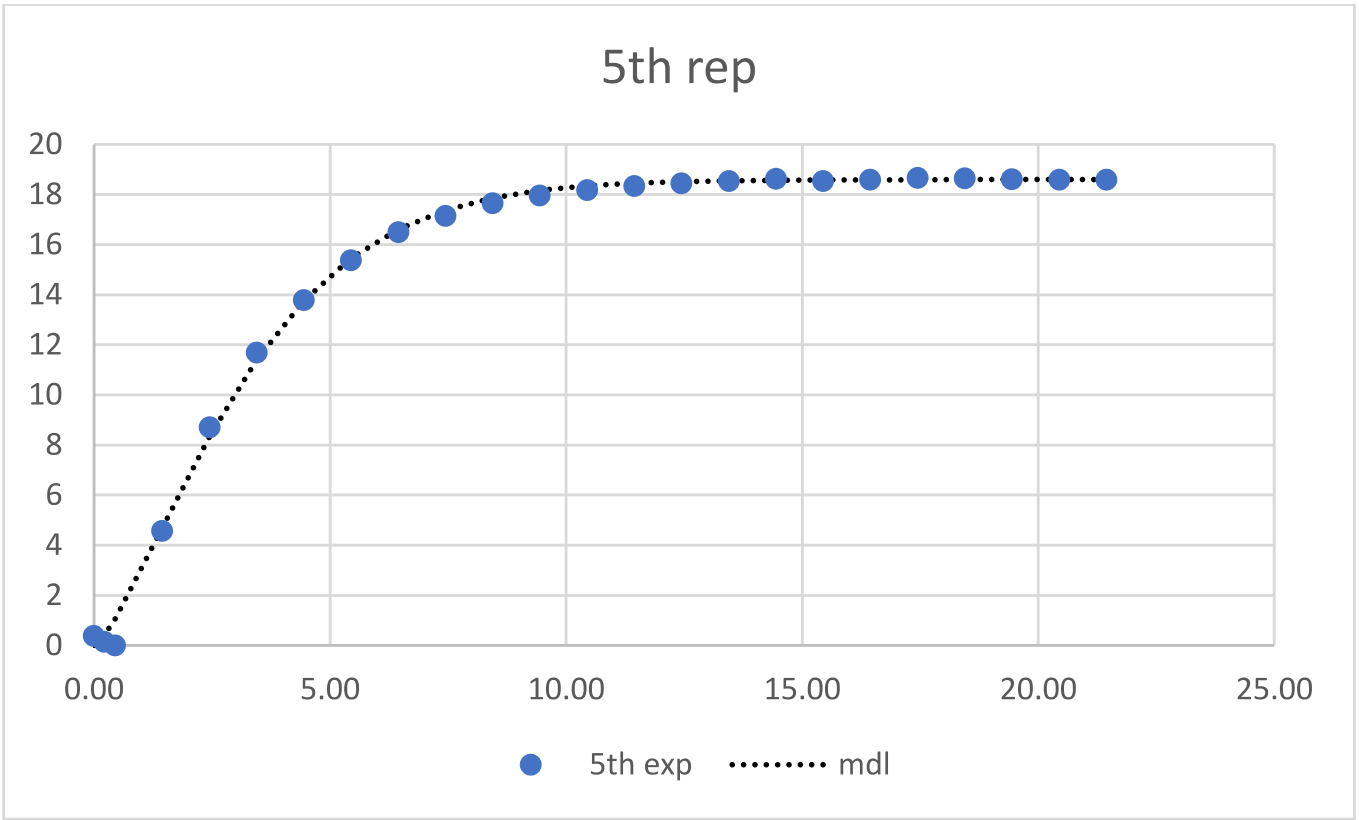


Figure 61 High temperature operation model rep 5

N°exp	Hours	t0	n	k
1	24	0	1.52	0.202
2	48	0	1.61	0.143
3	72	0	1.34	0.200
4	96	0	1.33	0.197
5	120	0	1.37	0.176

Figure 62 High temperature operation model parameters

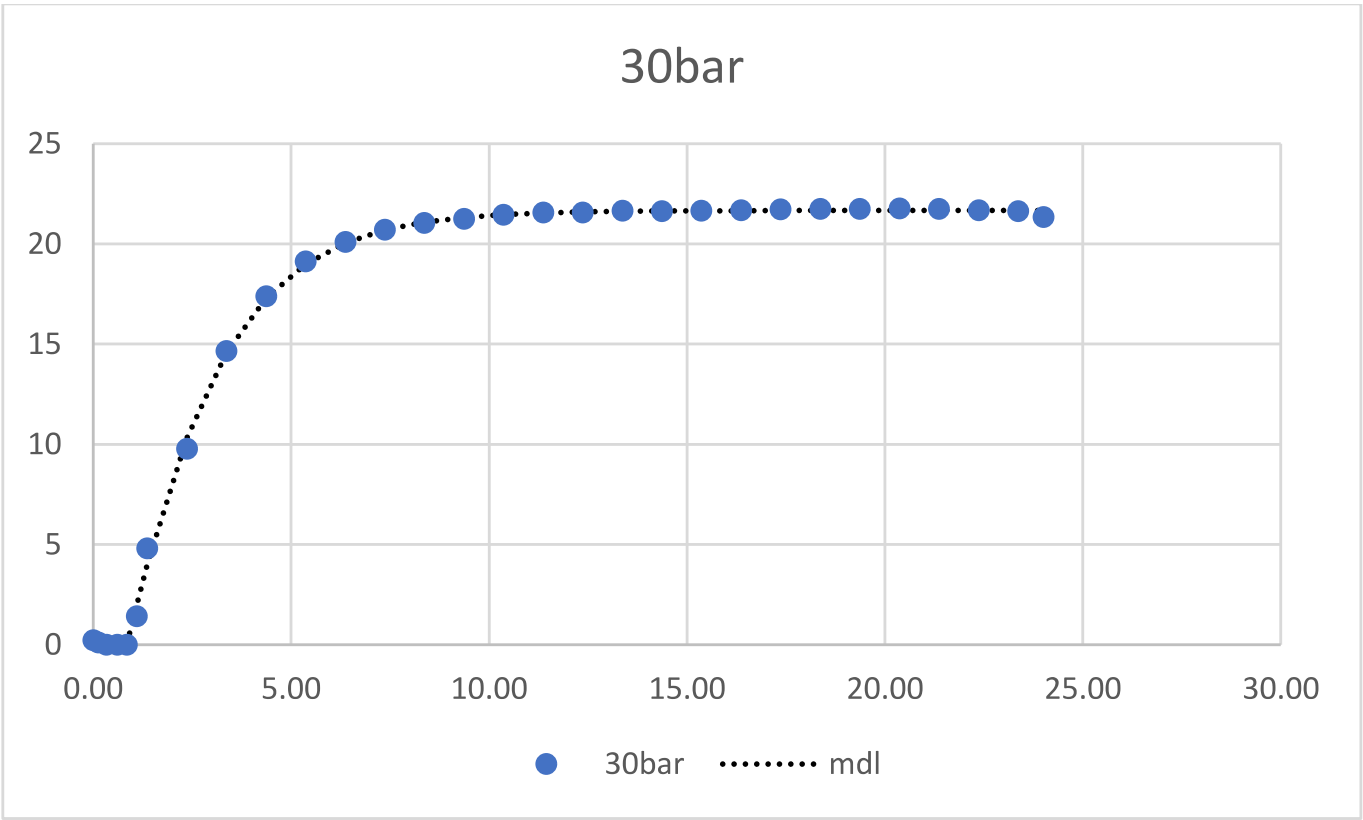


Figure 63 operation model 30 bar

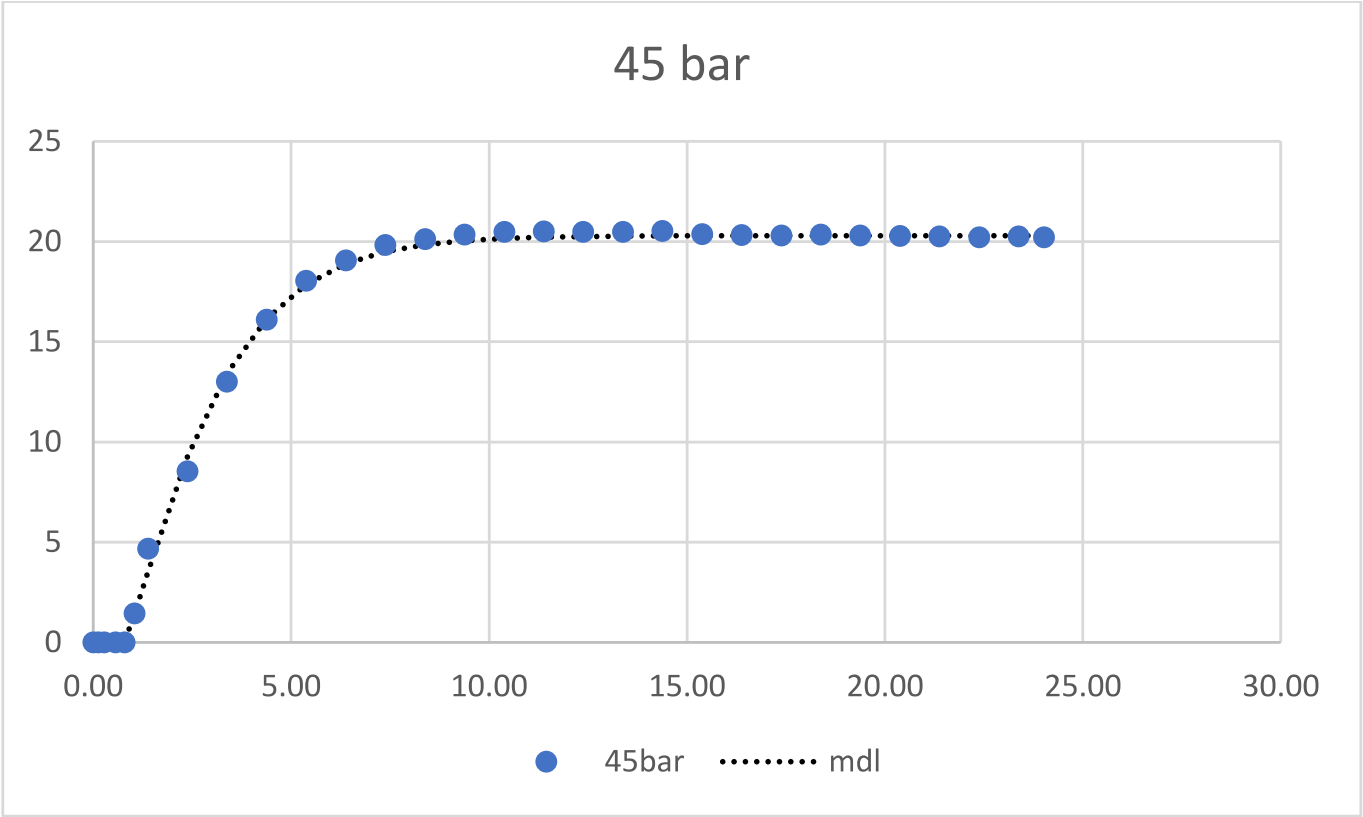


Figure 64 operation model 45 bar

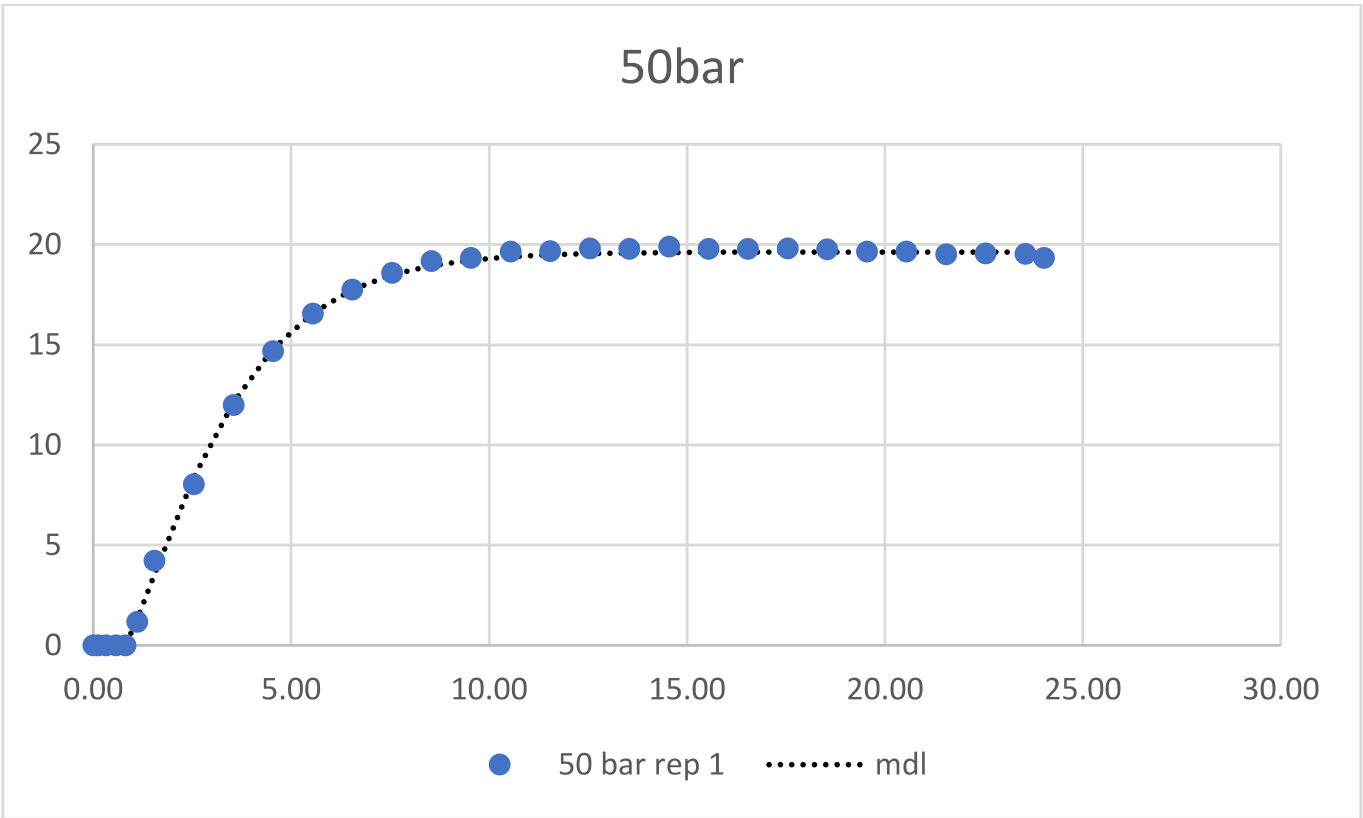


Figure 65 operation model 50 bar

exp	T0	n	k
30	0.847	1.08	0.412
45	0.785	1.18	0.352
50	0.814	1.20	0.289

Figure 66 operation model parameters for different pressures

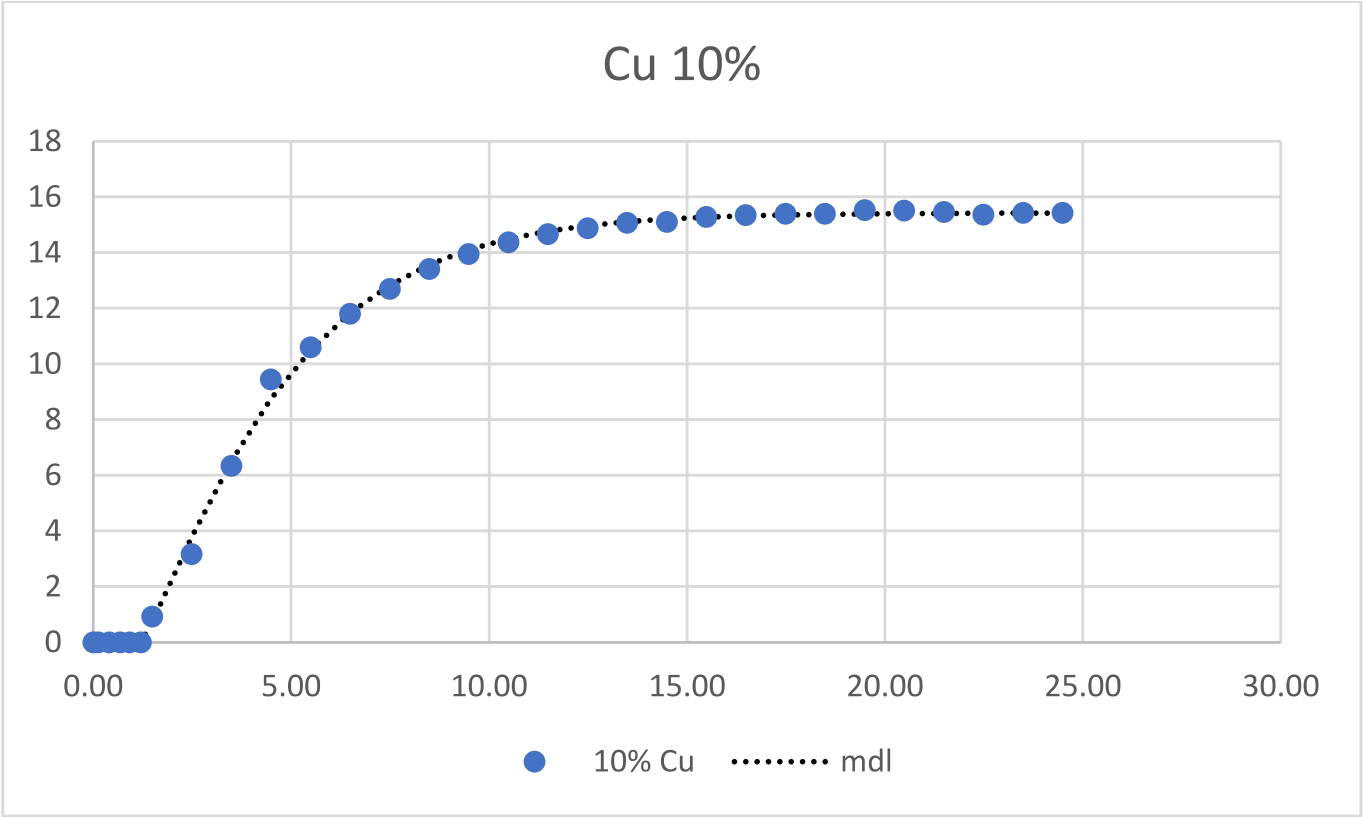


Figure 67 Adjusted model for catalyst at 10%Cu.

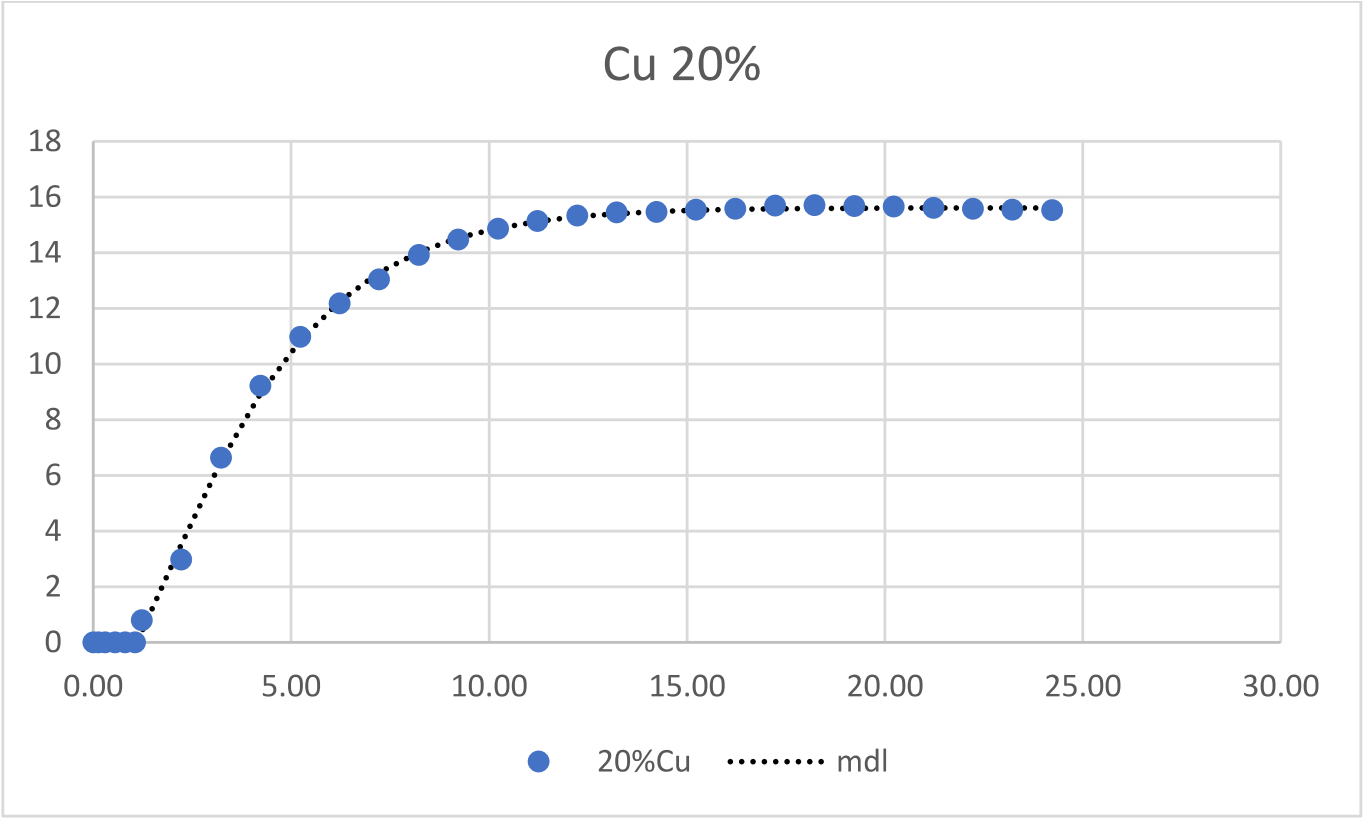


Figure 68 Adjusted model for catalyst at 20%Cu.

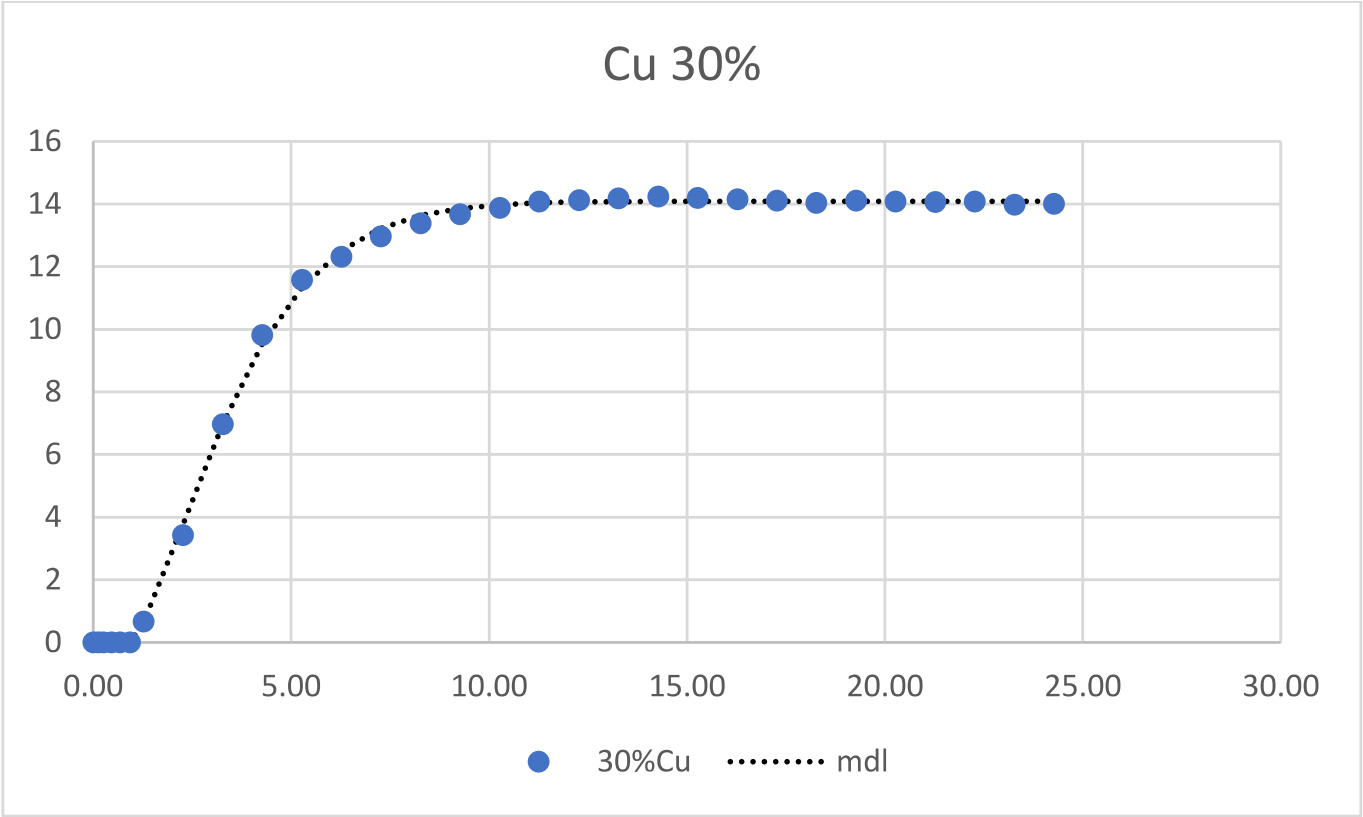


Figure 69 Adjusted model for catalyst at 30%Cu.

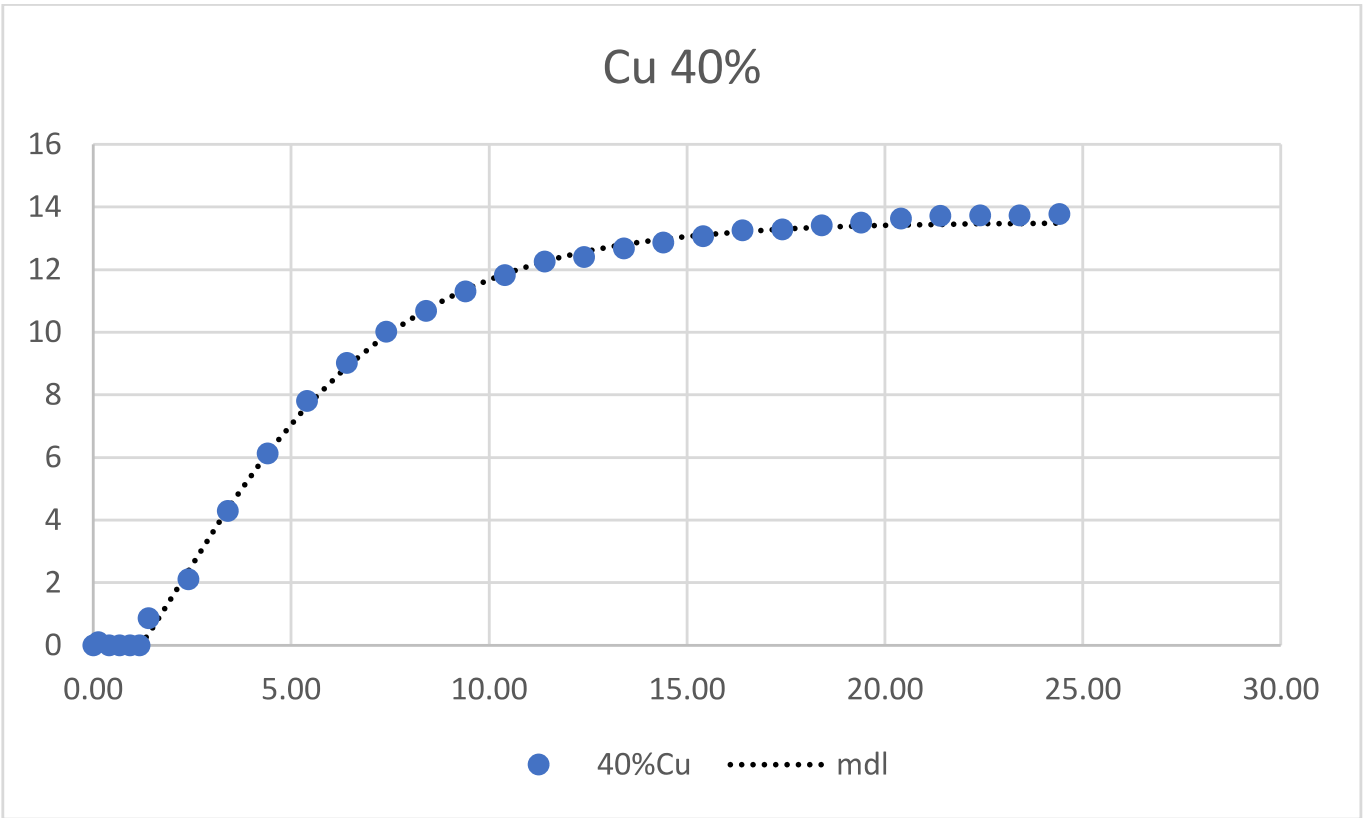


Figure 70 Adjusted model for catalyst at 40%Cu.

Cu %	t0	n	k
10%	1.201	1.16	0.209
20%	1.056	1.21	0.211
30%	0.921	1.42	0.203
40%	1.169	1.19	0.151

Figure 71 Adjusted model for catalysts parameters.

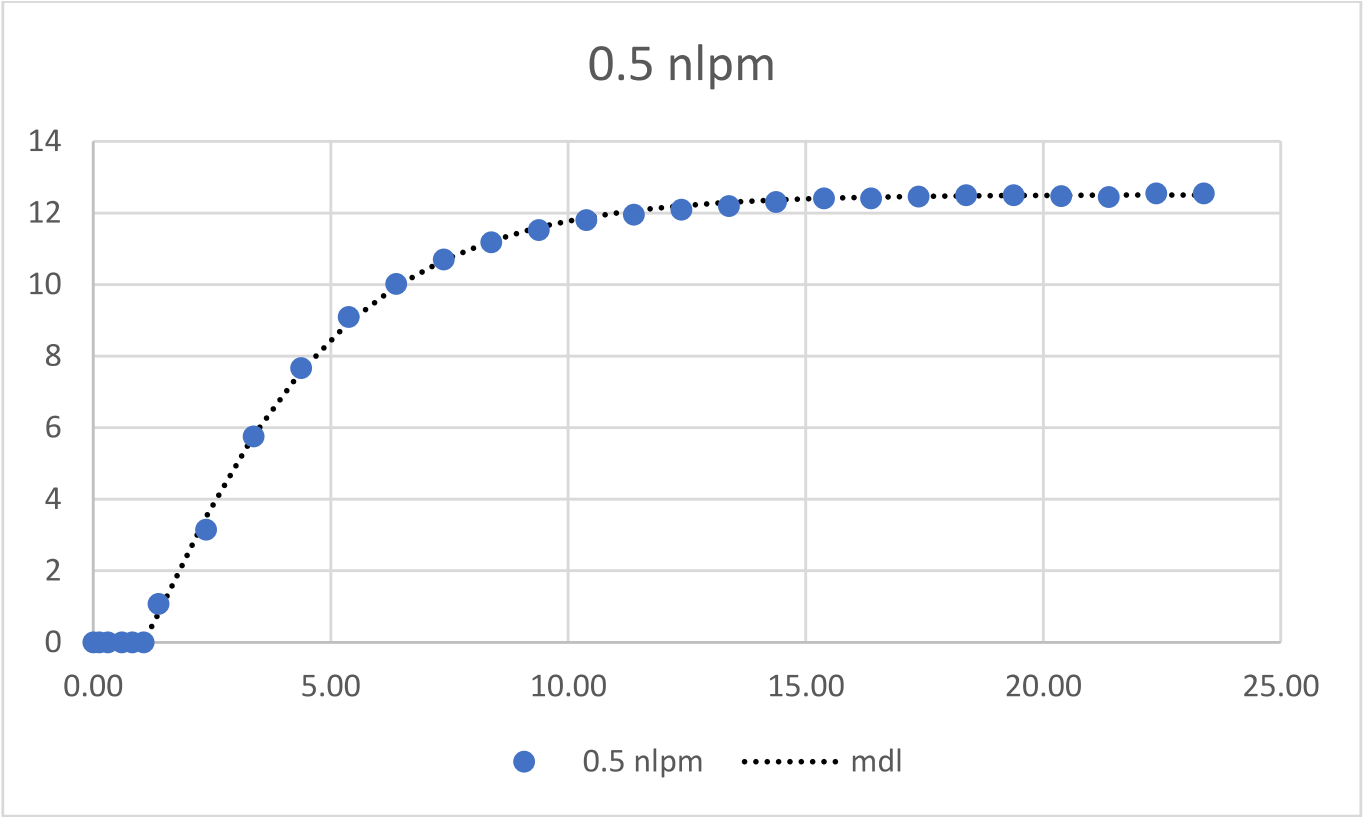


Figure 72 Adjusted model for 0.5 Nlpm.

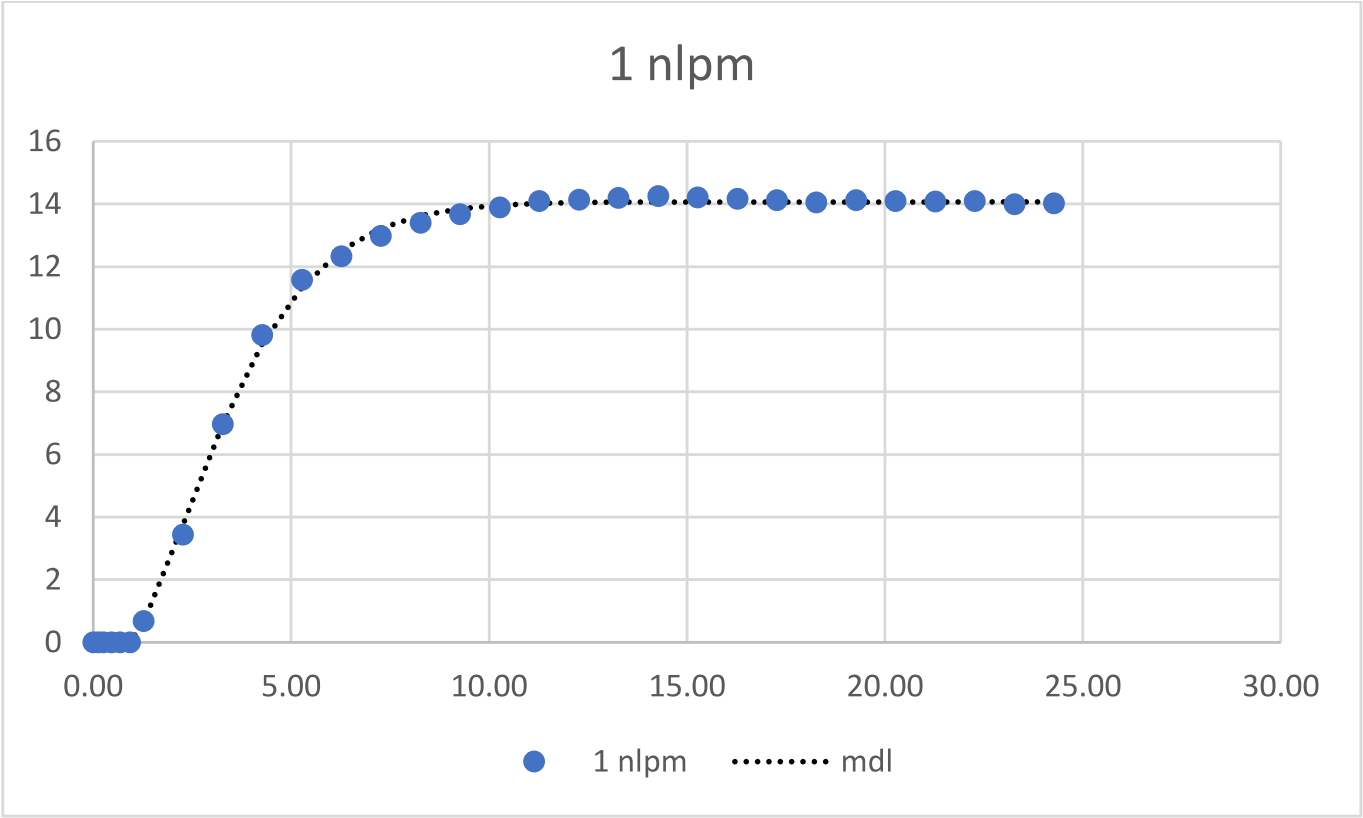


Figure 73 Adjusted model for 1 Nlpm.

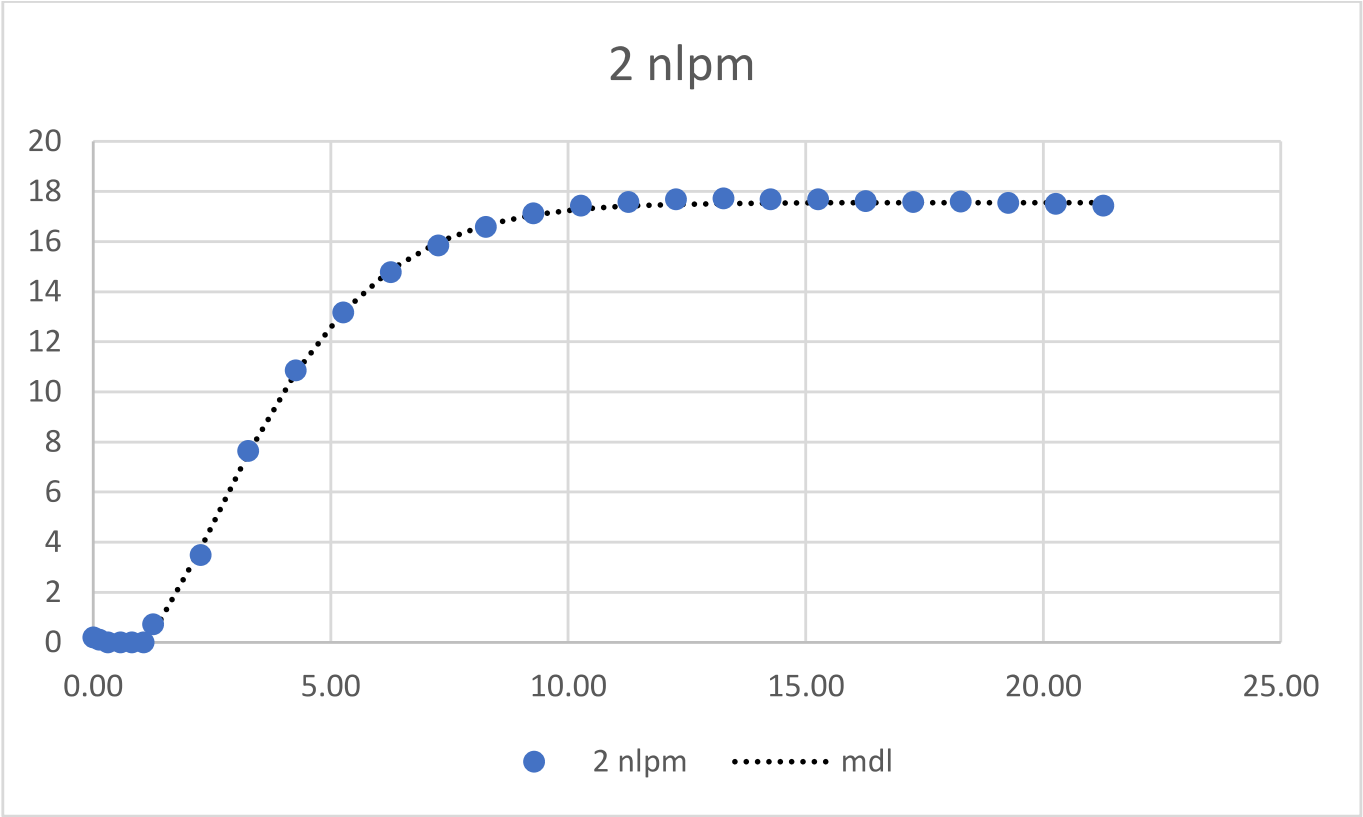


Figure 74 Adjusted model for 2 Nlpm.

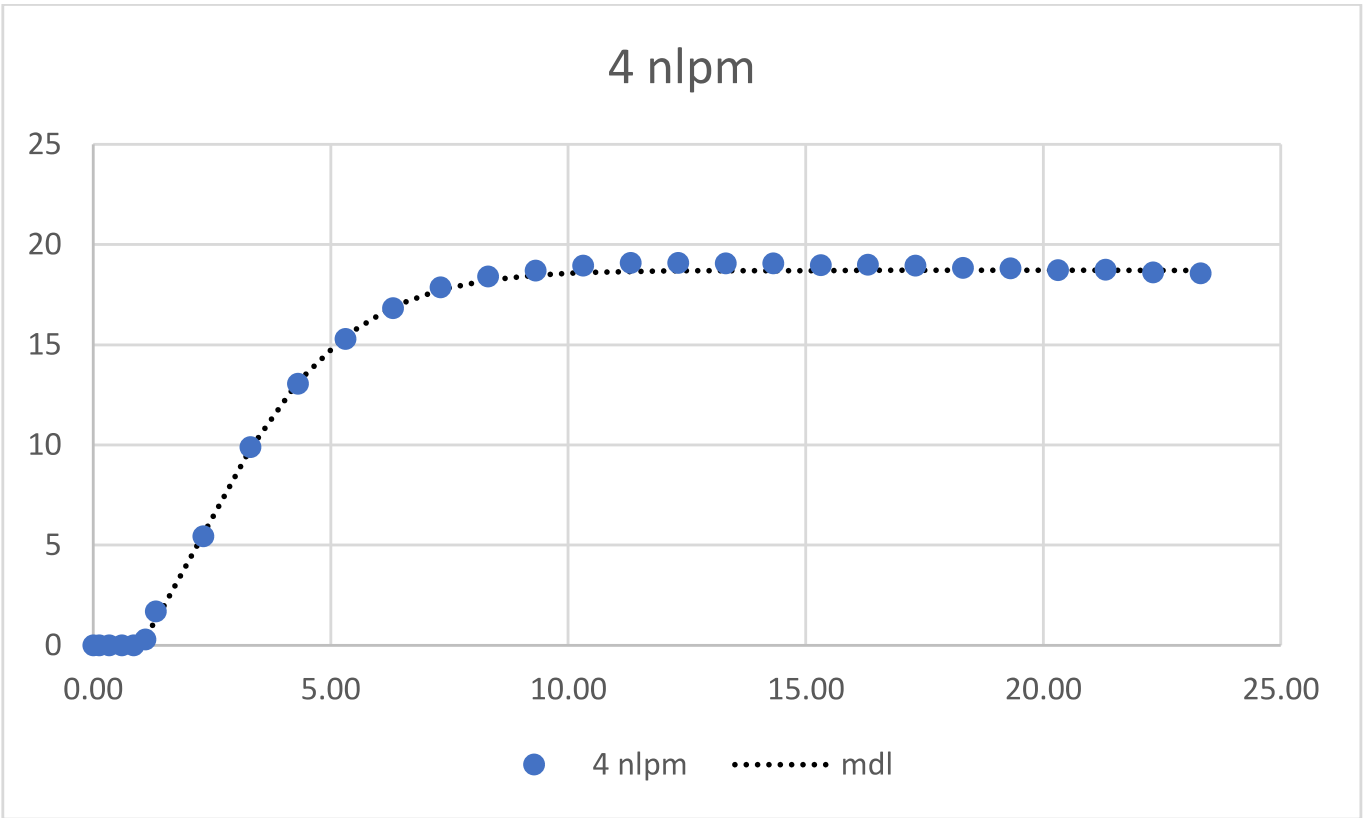


Figure 75 Adjusted model for 4 Nlpm.

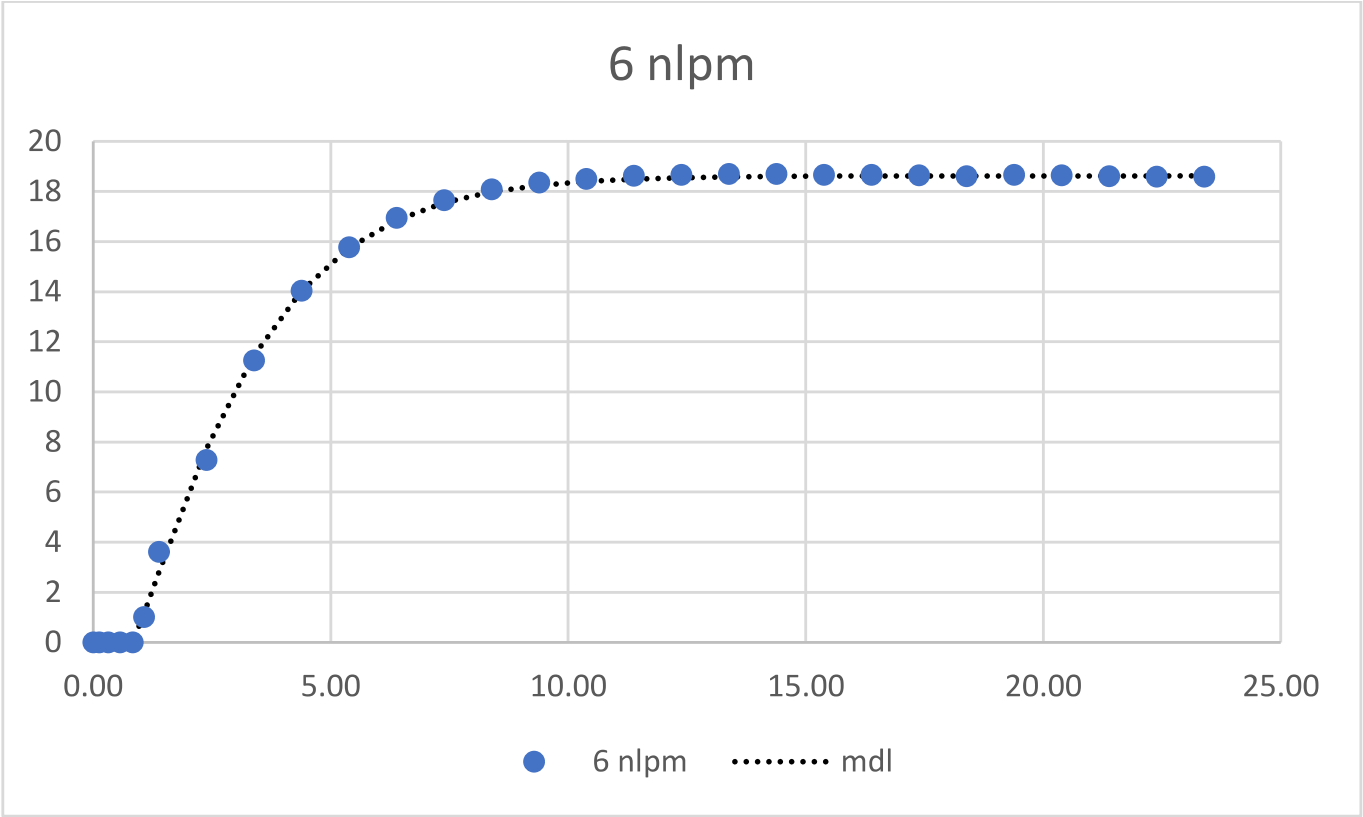


Figure 76 Adjusted model for 6 Nlpm.

C. load	t0	n	k
0.5	1.054	1.13	0.239
1	0.921	1.42	0.203
2	1.055	1.41	0.184
4	0.846	1.44	0.203
6	0.823	1.16	0.320

Figure 77 Adjusted model for circulating load parameters.