

# Mathematical investigations of a kinetic model for heterogenous catalysis of glycerol hydrogenolysis

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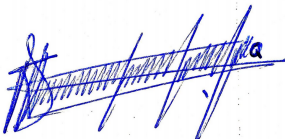
# Abstract

In this work we report on some mathematical investigations of the chemical process for the hydrogenolysis of glycerol over a heterogeneous metal catalyst. The main interest of this process is related to the fact that glycerol is produced as a by-product in the production of biodiesel in huge amounts that are expected to exceed the projected demands. This makes the sustainability of biodiesel production depend on the conversion of the glycerol into useful products hence it is a desirable goal to have effective conversion methods. A reaction model in a report of [Shozi et al. \(2017\)](#) is used to derive a system of ordinary differential equations (ODE) which is then analysed using methods from qualitative analysis of ODEs. Numerical solutions of the system are simulated to try and find out the solution's behaviour in the chemistry point of view. It was found that all solutions of the model converge to some stable limit point in a 2 dimensional plane in the positive cone of the  $\mathbb{R}^5$  space, and the limit point depends on the values of  $k_i$ 's as well as the hydrogen to glycerol ratios. Even though the results are based on a specific kinetic model, it is hoped that they may help in providing tools for better understanding and description of the reaction.

Key Words: Glycerol hydrogenolysis, Kinetics, Ordinary differential equations, Compartmental systems

## Declaration

I, the undersigned, hereby declare that the work contained in this research project is my original work, and that any work done by others or by myself previously has been acknowledged and referenced accordingly.



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Thandokuhle Quinton Ndlovu, 23 May 2019

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# 1. Introduction

The effects that climate change has on the environment cannot go unnoticed and as a result, has attracted researchers to find ways at which the situation remains controllable. Literature has pointed out that fossil fuels are one of the leading contributors to climate change due to their massive production of carbon dioxide, a gas reported to contribute massively to climate change (Pandhare et al., 2017). There exist various approaches to minimize the destructions caused by climate change which includes the use of biodiesel. This is a biofuel which hopes to decrease the absolute dependence on crude oil, one of the major contributors to climate change (ENERGY.GOV).

According to Zhao et al. (2019), during the production of biodiesel, another chemical called glycerol is produced in very large amounts and it is proposed that the production of glycerol will exceed its market demands in the near future. Glycerol has a lot of applications as it is used in the food industry, pharmaceuticals etc. In some work done by Torres et al. (2010), it is stated that even though the production of biodiesel has been commercialized, the tenability of this process depends on the conversion of glycerol into its useful chemical derivatives.

Therefore, there has been on-going research on how to convert the glycerol into suitable chemicals using different chemical methods and amongst those, hydrogenolysis is one of them, and it is briefly described in the following chapter. However in the work of Pandhare et al. (2017), it is reported that not much research on the kinetics underlying these reactions has been done. As a result in this study we seek to mathematically investigate the kinetics of a model for catalysed hydrogenolysis of glycerol using methods from the qualitative analysis of ODEs in an attempt to provide tools to describe and understand the reaction better. Numerical solutions to the model are simulated to try and understand the reaction's behaviour in the chemistry point of view as well as compare the model results to those obtained experimentally.

As steps towards this goal, we consider a reaction model in a report by Shoji et al. (2017) for the hydrogenolysis of glycerol using Cu-Re/ZnO catalyst, from which we derive a system of ODEs that governs the reaction. From the mathematical model, we aim to;

- analyse it using techniques from qualitative analysis of ODEs,
- perform numerical simulations of the model to compare with the experimental results and investigate the factors that affect the reaction,
- derive if possible, some general result(s) from the analysis about the reaction.

## 1.1 Order of work

In chapter 2 of this work, we look at the literature relevant to this work. This includes a brief summary on biodiesel production (a key process in glycerol production), the general result about the reaction and related models that have been reported. In Chapter 3 we present the specific chemical reaction of interest, the mathematical model and its basic properties and in Chapter 4 we present the mathematical analysis of the model. Finally, in Chapter 5 we present the results from the experimental data and numerical simulations, then the discussion and conclusion are given in Chapter 6.

## 2. Related Models

This chapter reviews some existing kinetic models on the hydrogenolysis of glycerol. However, for us to understand the mathematics behind the models, we first need to understand the chemical background of the process that results in the production of glycerol and the general result on the reaction for glycerol hydrogenolysis. We first look at the summary of the biodiesel production process, which consequently leads to the production of glycerol.

### 2.1 Biodiesel production

Biodiesel is produced mainly from animal fats and vegetable oil through a process called transesterification (Zhao et al., 2019). Figure 2.1 illustrates an outline of the processes involved in the production of biodiesel.

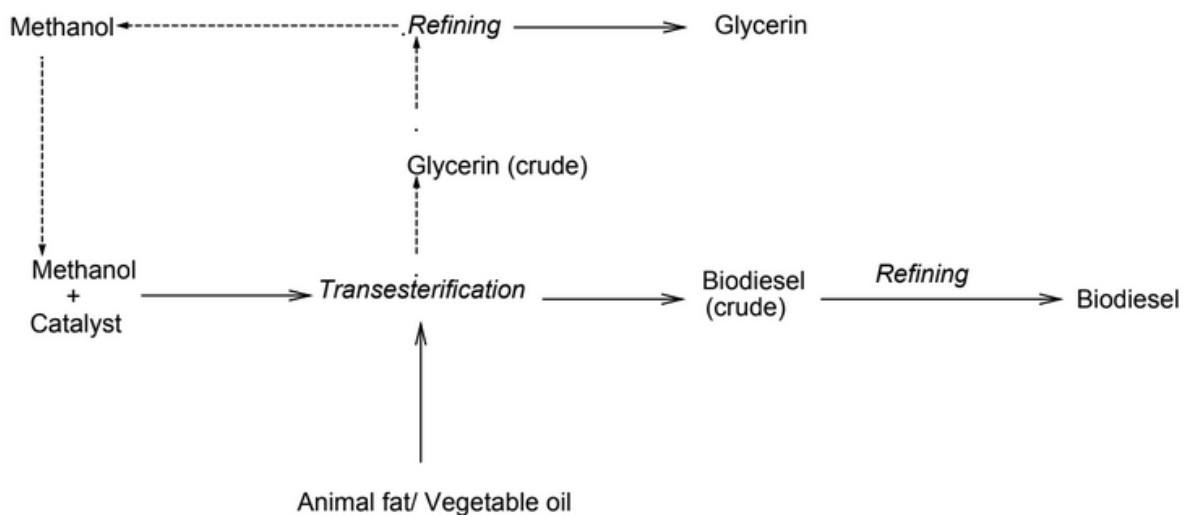


Figure 2.1: The biodiesel production process via transesterification (ENERGY.GOV).

In Figure 2.1 it can be seen that glycerin, commonly called glycerol is also produced. According to Shoji et al. (2016), for every 10 kg of biodiesel produced, 1 kg of glycerol is also formed as a by-product. Likewise, Zhao et al. (2019) reported that in 2016 the global production of biodiesel was approximately 32.8 million tonnes along with 3.28 million tonnes of glycerol as a by-product. This means that the sustainability and viability of commercializing the production of biodiesel lies on the utilization of glycerol (Torres et al., 2010).

It is therefore expected that with the increase in the production of biodiesel, more glycerol will be produced up to a point where the market cannot accommodate the excess. Lari et al. (2018) projects that by the year 2020, the production of glycerol will be 6 times more than the market demand. This is a cause for concern. As a result, studies on how to convert the glycerol into usable end products are of great interest (Shoji et al., 2016).

The physical and chemical properties of glycerol allows it to be used in numerous industrial applications (Wang et al., 2015). It has, therefore a variety of chemical applications, such as a blend in gasoline, coating in polymers, cosmetics, solvents, detergents, sweeteners and so on. Researchers have been involved in studies on how the glycerol can be converted effectively into its useful chemical derivatives. There are numerous methods used to convert glycerol into other useful chemicals, and this includes the use of catalysts alongside the accompanying reaction of interest such as etherification, esterification, fermentation, dehydration, hydrogenolysis etc, depending on the desired chemical products (Bozell and Petersen, 2010). For the purposes of this study, we focused on the hydrogenolysis reaction, which is briefly described in the next section.

## 2.2 General results on hydrogenolysis of glycerol

This is a reaction that involves the cleaving of chemical bonds of an organic substrate by hydrogen in the presence of a metal catalyst (Bozell and Petersen, 2010). When glycerol is hydrogenated in the presence of a catalyst, it leads to the production of 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD) and ethylene glycol (EG) as main products and other products such as ethanol, propanol and methane depending on the catalyst used. These main products have a lot of industrial applications such as being used as coolants, in manufacturing of fibre glass, in cosmetics as well as in ink production (Zhao et al., 2019). A general reaction scheme for the possible products of catalytic glycerol hydrogenolysis is shown below.

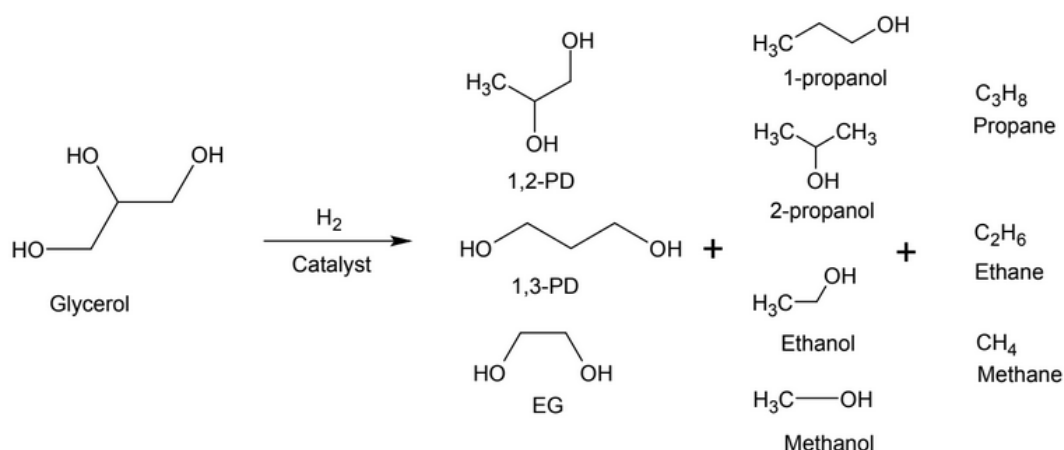
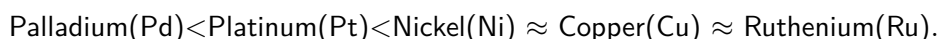


Figure 2.2: Main products from hydrogenolysis of glycerol (Wang et al., 2015).

Torres et al. (2010) stated that the hydrogenolysis of glycerol is a cost-effective process and makes use of readily available and renewable resources. The reaction results in a very complex reaction network which constitutes of both liquid and gas phase products. As a result, achieving a selective conversion to the desired products becomes a challenge. Research has been conducted on the effect of catalysts, temperature, pressure and concentrations of reactants in trying to improve the selectivity conversions to 1,2-PD and EG. Since reports have stated that the products from this reaction depend on the catalyst used, it has been reported by Torres et al. (2010) that the metal catalysts which plays a role in the

selectivity and conversions to 1,2-PD and EG are in the order;



Although Ru is the better catalyst, it favours the production of gaseous rather than liquid phase products. As a result, most reports are on bimetallic catalysts which have been found to improve the production of the liquid products (Torres et al., 2010).

We have looked at the chemical background of the entire process that leads to the production of glycerol. Before we present some models related to the reaction, we first look at some basic concepts that are used when modelling chemical reactions.

## 2.3 Modelling chemical reactions

Given a chemical system, that is well mixed and closed, kinetic equations that depicts the changes in concentrations of both the reactants and products can be derived. These equations can be presented as; continuous time Markov chains or system of differential equations, giving rise to the kinetic model of the system.

Both models have some advantages, but for purposes of this work we focused on kinetic models involving the differential equations because the model's initial conditions and the kinetic parameters completely determines the system's future state, with no randomness involved. Also, according to Cain (2014) it is easy to set the differential equations by simply invoking the law of mass action, which is briefly described in the following section alongside the principle of conservation of mass.

**2.3.1 Principle of conservation of mass.** The principle states that for any closed system, the rate of change in its mass remains constant (Kelly P, Solid Mechanics Lecture Notes). This means that, for a species of mass  $m$  in a well defined system, we have that

$$\frac{dm}{dt} = 0.$$

**2.3.2 Law of mass action.** This law states that the rate of an elementary chemical reaction is proportional to the reactant's concentrations raised to the power of the stoichiometric equations (Baird, 1999). In general, consider the irreversible reaction where species  $X$  reacts with  $Y$  to give  $Z$ ,



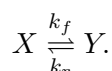
The law of mass action states that the rate of this reaction can be given by

$$r = k[X]^a[Y]^b.$$

where  $[X]$ ,  $[Y]$  denotes the concentration of reactants,  $a, b$  are the stoichiometric coefficients and  $k$  is the rate constant. Given any chemical reaction, its kinetic model can be derived using the basis of the mass action law. For simplicity, we use only symbols, say  $X$ , rather than  $[X]$  to represent the concentrations of species involved.

As a simple example let us consider a reversible reaction where  $X$  is converted to  $Y$  with the assumption that for both the forward and reverse reaction, the molecules of  $X$  do not interact with each other and

also those for  $Y$ . Then we have



Using the mass action law, the kinetic model for this system can be given as

$$\begin{aligned}\frac{dX}{dt} &= -k_f X + k_r Y \\ \frac{dY}{dt} &= +k_f X - k_r Y\end{aligned}$$

These system of differential equations can be solved for concentrations of both  $X$  and  $Y$  using given initial conditions and kinetic parameters. In the above case the solution  $(X(t), Y(t))$  can be obtained explicitly because the system of ordinary differential equations is linear and autonomous (Barreira and Valls, 2012). In more complicated cases, where in the law of mass action the powers are not all equal to 1, the system of rate equations is no longer linear and its study requires the use of numerical methods or other types of approximation techniques, such as qualitative theory methods, asymptotic methods, etc.

Since we have seen that it is possible to derive a kinetic model for a system of chemical reactions, we then present some models that have been reported on the hydrogenolysis of glycerol, assumptions made and derive some conclusions from them.

## 2.4 Power law model

We first look at the underlying principles of the power law model before we proceed and look at the work done by Pandhare et al. (2017).

**2.4.1 Principles of the model.** Based on the principle of the mass action law, for a chemical reaction



the reaction rate  $r_i = -\frac{dC_i}{dt}$  is expressed by

$$r_i = f(T) \cdot g(C_i), \quad (2.4.1)$$

where  $T$  is the temperature,  $C_i$  is the concentration of reactant  $i$  and, according to the Arrhenius law

$$f(T) = A e^{-\frac{E}{RT}}, \quad (2.4.2)$$

where  $A$  is the frequency factor,  $E$  is the activation energy,  $R$  is the gas constant,  $T$  is the temperature (Fogler, 2017). Assuming that the temperature is constant, the coefficient  $f(T)$  of the rate equation is a constant  $k$ . The function  $g$  in Equation (2.4.1) is, in the power law model, a power law

$$g(C_i) = C_i^r,$$

where  $r > 0$  is a constant. It must be noted that in the case of elementary chemical reactions, the power  $r$  is a positive integer, according to the law of mass action.



**2.4.2 Pandhare et al.(2007) work.** Using the principles of the power law model, Pandhare et al. (2017) developed a model for the hydrogenolysis of glycerol which exhibited a positive correlation when compared with the experimental findings.

In developing the model, they took the reaction of Glycerol (G) in the presence of a catalyst (S) to be irreversible, i.e



Now, by the power law model, it follows that the rate of disappearance of glycerol can be given by

$$\frac{dC_G}{dt} = -kC_G^n, \quad (2.4.4)$$

where  $C_G$  is the concentration of glycerol at any given time,  $n$  is the reaction order and  $k$  is the temperature dependant rate constant given in Equation (2.4.2).

Then Equation (2.4.4) was solved numerically and to obtain an optimum value of the kinetic parameters, optimization techniques were used. The order of reaction was found to be 1.2, thus showing that the hydrogenolysis of glycerol is not an elementary reaction (Lahr and Shanks, 2003). This means that, according to Pandhare et al. (2017), a more complicated chemical mechanism which takes into account some of the important steps of the reaction like adsorption and desorption by the catalyst has to be investigated, hence the need for a much detailed model as we shall see in the next section.

## 2.5 Langmuir-Hinshelwood-Hougen-Watson model (LHHW)

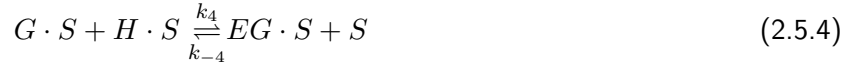
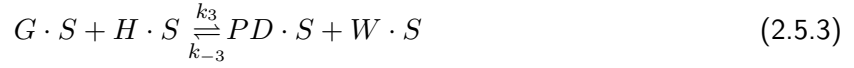
The Langmuir-Hinshelwood-Hougen-Watson (LHHW) is a commonly used model to express the rates for heterogeneous reactions. To develop this model, in a report by Pandhare et al. (2017) the glycerol was treated as the limiting reactant, which implied that the hydrogen was in excess and its pressure was considered to be constant in the presence of a 35% Cu-MgO catalyst.

A 3-step reaction mechanism was used where, in the first step, Glycerol(G) get adsorbed in the surface of the catalyst(S) as well as the hydrogen(H). The second step involves the surface reaction between the adsorbed glycerol and hydrogen to give 1,2-PD (which we represent as PD) and EG. In the last step, both the PD and EG are desorbed resulting into the regeneration of the catalyst (Pandhare et al., 2017). A more general mechanism for the reaction is shown next.

Adsorption



Surface reaction



Desorption



Deriving the rate equations from Equations (2.5.1) to (2.5.6); taking the surface reaction step to be irreversible (i.e.  $k_{-3} = 0 = k_{-4}$ ) and as the rate determining step, and assuming that the adsorption and desorption steps are at equilibrium, the rate equations simplified to

$$r_3 = -k_3 \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} C_G P_H C_S^2 \quad (2.5.7)$$

$$r_4 = -k_4 \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} C_G P_H C_S^2. \quad (2.5.8)$$

Here, Equations (2.5.7) and (2.5.8) represents the rate of the parallel reactions for the conversion of glycerol to PD and EG respectively,  $C_G$  and  $C_S^2$  are the concentrations of glycerol and catalysts at any time  $t$  and  $P_H$  is the partial pressure for the hydrogen. Considering the fact that there is adsorption taking place in the catalyst, the site balance was evaluated as

$$C_{tot} = C_S + C_{G \cdot S} + C_{PD \cdot S} + C_{EG \cdot S} + C_{H \cdot S}. \quad (2.5.9)$$

Using Equation (2.5.9), and substituting the rate equations it follows that

$$C_S = \frac{C_{tot}}{1 + k_1/k_{-1} C_G + k_2/k_{-2} P_H + C_{PD}/(k_5/k_{-5}) + C_{EG}/(k_6/k_{-6})}. \quad (2.5.10)$$

Eventually the rate equations for the production of 1,2-PD and EG reduced to

$$r_3 = \frac{-k_3 K_1 K_2 C_G P_H C_{tot}^2}{1 + K_1 C_G + \frac{C_{PD}}{K_5} + K_2 P_H + \frac{C_{EG}}{K_6}}, \quad (2.5.11)$$

$$r_4 = \frac{-k_4 K_1 K_2 C_G P_H C_{tot}^2}{1 + K_1 C_G + \frac{C_{PD}}{K_5} + K_2 P_H + \frac{C_{EG}}{K_6}}. \quad (2.5.12)$$

The unknown parameters of the above system were estimated by using optimization techniques. Pandhare et al. (2017) disclosed that simulations by the model gave consistent results with those determined experimentally.

Nonetheless, the report on this model is a rough generalization of the reaction, in the sense that it predicts only 2 products yet reports showed that the reaction produces a variety of products in different phases, hence the need for a much detailed model, which more or less depicts how the reaction proceeds chemically. In the section below, we look into some models which took into account the complex nature of the reaction. However, it must be noted that most of the models reported in this reaction invoked both the concepts of the power law and LHHW model.

## 2.6 Other models

Torres et al. (2010) reported on the kinetic model on the hydrogenolysis of glycerol using Ru-Re/C catalyst. Since the reaction results into a complex chemical network, they made use of the Ru-Re/C catalyst which helps in reducing the number of gaseous products formed. A series of experiments were performed at different temperatures, initial hydrogen pressures and catalyst concentrations.

Rather than developing a model that takes into account only 1,2 PD and EG as products, their model took into account both the gaseous and liquid phase products in an attempt to investigate the kinetics of the reaction and understand its selectivity so it can be improved. Their kinetic model was developed based on the products (liquid and gaseous) shown in Figure 2.3 below. The detailed reaction scheme of Figure 2.3 is found in a report by Torres et al. (2010).

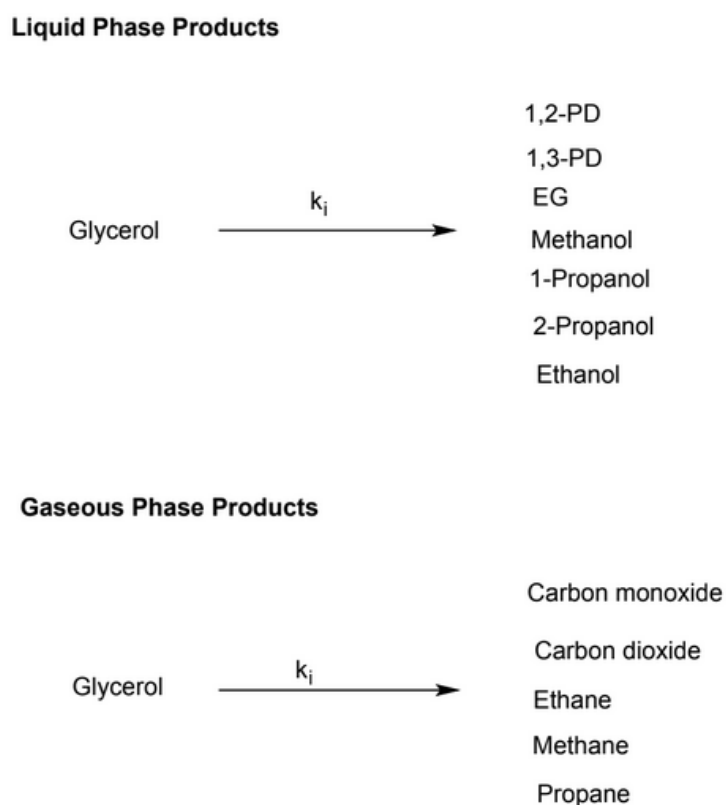


Figure 2.3: Liquid and gas phase products for glycerol hydrogenolysis using Ru-Re/C catalyst (Torres et al., 2010).

In this model, when representing the amount of hydrogen gas used, they invoked concepts from Henry's law. From Henry's law we know that the amount of gas dissolved in a solvent, under isothermal conditions, is directly proportional to the partial pressure of the gas that is in equilibrium with the solvent, that is

$$C_{gas} = K_H P_{gas},$$

where  $C_{gas}$  is the amount of gas dissolved,  $K_H$  is Henry's constant and  $P_{gas}$  is the partial pressure of the gas. So, using both Henry's and the mass action law, they were able to derive rate equations for the products in Figure 2.3. For example, the rate equation for product  $i$  was expressed as

$$r_i = x k_i C_G \frac{C_H}{K_H},$$

where  $C_G$ ,  $C_H$ ,  $x$  are the concentrations of glycerol, hydrogen, catalyst respectively and  $K_H$  is the Henry's constant. In a similar way, the other rate equations were derived and they had a 12 dimensional system. This model constitute both the gaseous and liquid phase products and it was solved numerically together with optimization techniques to obtain the rate parameters. The simulations from the model correlated well with the experimental data and it predicted that there is higher selectivity to 1,2 PD and propanol compared to all the other gaseous and liquid phase products when using the Ru-Re/C catalyst, just like the experimental results (Torres et al., 2010).

This model depicted somehow the exact reaction network taking place in the hydrogenolysis of glycerol and this shows that even the most complex reaction can be kinetically modelled. However, in the report of Torres et al. (2010), there is no detailed analysis of the model kinetics towards selectivity to EG, which has been reported as one of the major products and other products. Results produced focused on 1,2 PD and propanol, hence more interpretation of the results from the model are a necessity so to have a better understanding of the kinetics for the reaction.

Jin et al. (2016) also reported on a kinetic model for the hydrogenolysis of glycerol using Pt/C catalyst with in situ formed hydrogen. By in situ, we mean hydrogen that is produced within the reaction chamber and used for the hydrogenolysis rather than the one from external sources. Even though the model followed assumptions similar to the one formulated by Torres et al. (2010), the findings are some how different. The model showed that, using in situ formed hydrogen reduces the amount of gaseous products as a result, it favours the production of the liquid products like 1,2-PD, EG and others. However, the report on the model does not give more details on the selectivity to specific liquid products, but rather generalizes on the production of liquid phase products.

From the above reported models, one can see that the power law model does not show the much detailed steps of the entire reaction as well as the LHHW model, which only focuses on 1,2-PD and EG as products yet there are other species formed. Also, the model derived from Figure 2.3 even though it involves both gaseous and liquid phase products, it contains a lot of intermediates and gives rise to a 12 dimensional system with a lot of parameters when being modelled. It is for that reason as we shall see later on, that we use a scheme proposed by Shoji et al. (2017) which contains few intermediates and gives rise to a system of much lesser dimensions while it also takes into account both gaseous and liquid phase products.

As a result, in this study we seek to investigate the underlying kinetics of the reaction using methods from the qualitative analysis of ODEs, so we can have tools to better describe and understand the reaction so that the yield of the liquid phase products can be maximised. In the next chapter, we present the chemical reaction used alongside the derived mathematical model with its basic properties.

## 3. The Chemical Problem, Mathematical Model and its basic properties

In this chapter we discuss the chemical problem in terms of its reaction mechanism and the experimental results, then formulate the mathematical model using ordinary differential equations. We use a scheme by [Shozi et al. \(2017\)](#) to formulate the model since we have the experimental data that accompanies the scheme, making it possible to compare the model simulations with experimental results as well as estimate the reaction parameters. We start with a brief summary of the reaction, focusing mainly on the mechanism and the experimental results.

### 3.1 Reaction mechanism

Chemists have reported on the different reactions that have been studied for the catalytic hydrogenolysis of glycerol, however for purposes of this study we consider one reaction reported by [Shozi et al. \(2017\)](#). This reaction involves the use of a Cu-Re/ZnO catalyst, hydrogen and glycerol as the main reactants and the reaction is carried at suitable temperatures, around  $250^{\circ}\text{C}$  and hydrogen pressure of 60 bar ([Shozi et al., 2017](#)).

**3.1.1 Adsorption.** The reaction involves the use of a metal catalyst where glycerol and hydrogen get adsorbed on the catalyst's site. Then, the adsorbed species react forming the products while regenerating the catalyst ([Pandhare et al., 2017](#)).

**3.1.2 Reaction scheme.** Since the reaction results into a complex network of parallel reactions, different gaseous and liquid phase products are obtained. [Shozi et al. \(2017\)](#) proposed a reaction mechanism for possible pathways of glycerol hydrogenolysis. The reaction proceeds through the initial formation of glyceraldehyde, glycolaldehyde and formic acid as intermediates through the removal of hydrogen from the glycerol. Further hydrogenolysis then gives the products, mainly ethylene glycol, methanol and carbon monoxide depending on the catalyst used. A detailed mechanism for the reaction is presented in [Figure 3.1](#).

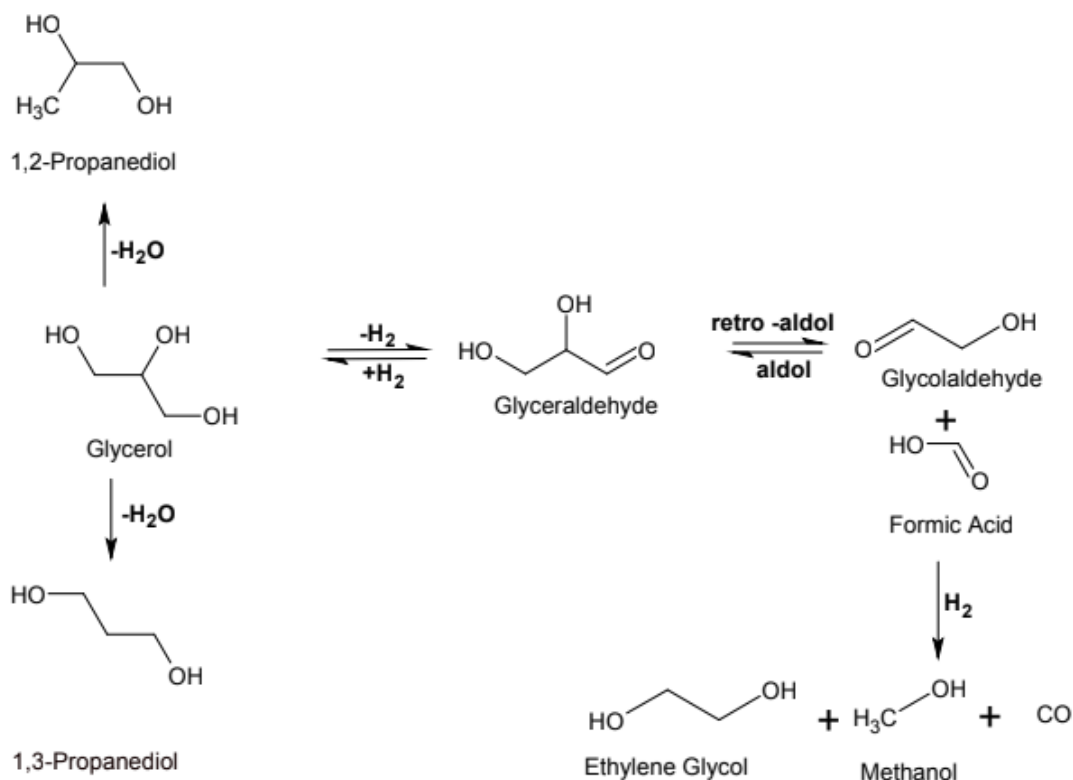


Figure 3.1: Reaction mechanism for the conversions of glycerol over Cu-Re/ZnO catalyst (Shozi et al., 2017).

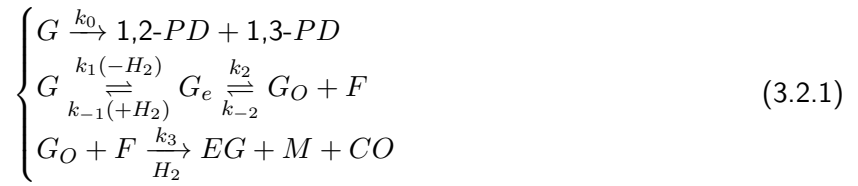
From the proposed mechanism, it is believed that retro-aldol conversion of glyceraldehyde is the main path for the formation of  $\text{C}_{1-2}$  molecules like EG and methanol. Also, the formed 1,2-PD can be decomposed further into EG using suitable experimental conditions. At the end of the reaction they had 2 layers; an aqueous and an organic layer. The organic layer was analysed for products using Gas Chromatography (GC) instruments. The gases collected were also analysed using GC instruments and concentrations of products were determined and recorded.

However, due the Cu-Re/ZnO catalyst used in the experiment of Shozi et al. (2017), it was reported that the 1,3-PD and the carbon monoxide were produced in very small amounts compared to the EG and 1,2-PD, and the methanol was around 25% of the EG. It was also reported that increasing the amount of hydrogen results in an increase in the production of EG over 1,2-PD. In a similar way, decreasing the amount of hydrogen resulted in a decrease in EG produced over 1,2-PD.

Having looked at the reaction and the experimental results, in the next section we present the mathematical model derived from the mechanism and its basic properties.

## 3.2 Model development

A more compact way of writing the chemical reactions network depicted in Figure 3.1 is the following;



where  $G_e$  is glyceraldehyde,  $G_O$ - glycolaldehyde, F- formic acid, M- methanol and CO is carbon monoxide. We use the notation PD to represent 1,2-PD as we shall see in the following sections. From the reaction mechanism, we have that the intermediates are  $G_e$ ,  $G_O$  and F since these are the only species that are produced first then later consumed.

For simplicity of the model, we introduce some new notation for each of the species involved in the reaction. It must be noted that we took  $G_O = F$ , and this is justified in the following chapter in Equation (4.0.1).

Old Notation	New Notation
$G$	$X_1$
$G_e$	$X_2$
$G_O = F$	$X_3$
$EG$	$X_4$
$PD$	$X_5$

Table 3.1: Simplified notation for the chemicals.

Assuming the validity of the mass action law, a system of differential equations is derived from (3.2.1) and it is shown below.

$$\begin{aligned} \frac{dX_1}{dt} &= -k_0X_1 - k_1X_1 + k_{-1}H_2X_2 \\ \frac{dX_2}{dt} &= k_1X_1 - k_{-1}H_2X_2 + k_{-2}X_3^2 - k_2X_2 \\ \frac{dX_3}{dt} &= k_2X_2 - k_{-2}X_3^2 - k_3H_2X_3^2 \\ \frac{dX_4}{dt} &= k_3H_2X_3^2 \\ \frac{dX_5}{dt} &= k_0X_1 \end{aligned} \quad (3.2.2)$$

where we use now the notation  $X_1, X_2, X_3, X_4, X_5$  to denote the *concentrations* of; glycerol, glyceraldehyde, glycolaldehyde/formic acid, ethylene glycol and 1,2-PD respectively. It must be noted that from the reaction given by (3.2.1), it is seen that the rate of production of 1,3-PD is the same as that of 1,2-PD, however, experimentally it is not the case. Actually relatively small amounts of 1,3-PD were obtained, similarly with CO. These cases, together with that of methanol are somehow the limitations

of the model by [Shozi et al. \(2017\)](#), since they cannot be represented mathematically using the ordinary differential equations. It is believed that this is due to the fact that the reaction has a lot of side reactions, as a result getting the exact chemical model becomes a challenge.

We now present some basic properties of the model together with a brief description on how the parameters were estimated.

**3.2.1 Assumptions.** To develop the kinetic model, it is assumed that the pressure of hydrogen and the catalyst's concentration in the reaction are constant ([Sharma et al., 2014](#)).

**3.2.2 Initial conditions.** The initial conditions for the reaction is 0 for all the species except for glycerol and hydrogen, i.e the initial conditions are

$$(X_1, X_2, X_3, X_4, X_5)(0) = (X_1(0), 0, 0, 0, 0), \quad (3.2.3)$$

where  $X_1(0) > 0$ .

**3.2.3 Parameters.** The rate constants of the model were determined using experimental data from the report of [Shozi et al. \(2016\)](#) and then compared using parameters in the report of [Jin et al. \(2016\)](#). In determining the rate constants, first the Turn Over Frequency (TOF) of the catalyst was determined with guidance from the report of [Zhao et al. \(2019\)](#) and then using Arrhenius plots, the order of the reaction was investigated by plotting the logarithm of TOF versus the inverse of temperature.

Reports for these plots with different catalysts used have linear plots and this shows that the reaction is first order ([Mondal et al., 2019](#)). Hence assuming the validity of the mass action law, the reaction's integrated rate law can be determined and a plot of the logarithm of glycerol concentration against time is obtained. The slope of this plot is the estimate of the rate constant.

In Table 3.2 below we present their orders of magnitude.

Parameter	Order of Magnitude
$k_0$	$\leq 10^{-1}$
$k_1$	$\leq 10^1$
$k_{-1}$	$\leq 10^1$
$k_2$	$\leq 10^3$
$k_{-2}$	$\leq 10^3$
$k_3$	$\leq 10^3$

Table 3.2: Orders of magnitude for the reaction constants obtained using experimental data.

Having derived the mathematical model, we then use some techniques from the qualitative analysis of ODEs to analyse the model as we shall see in the following chapter.



## 4. Mathematical Analysis

In this chapter we present some mathematical analysis of the model, mainly its equilibria, properties of the solutions and their stabilities. We start by justifying that  $G_O = F$  as indicated in Table 3.1.

It must be noted that in the chemical process  $G_O = F$ , hence  $G_O$  is used to represent both. This is because they are both intermediate chemical species that are absent at the start of the reaction and are produced and consumed always in equal amounts in reactions (3.2.1).

Mathematically this claim that  $G_O = F$  is proved as follows;

From (3.2.1), assuming the mass action law we have

$$\begin{aligned}\frac{dG_O}{dt} &= k_2 G_e - k_{-2} G_O F - k_3 G_O F H_2 \\ \frac{dF}{dt} &= k_2 G_e - k_{-2} G_O F - k_3 G_O F H_2\end{aligned}$$

The difference of the two gives

$$\frac{d}{dt}(G_O - F) = 0$$

which upon integrating gives

$$G_O = F + (G_O - F)(0). \quad (4.0.1)$$

Since  $(G_O - F)(0) = 0$  from the initial conditions and because both these intermediate chemical species are absent at the start of the reaction, we conclude from Equation (4.0.1) that  $G_O(t) = F(t)$  for all time  $t \geq 0$ .

We then proceed by presenting an analysis of the nature of the solutions to the model as shown in the next section.

### 4.1 Solutions to the equations

We start by stating that the Cauchy problems for the system given by Equation (3.2.2) have unique solutions. As a consequence, we introduce a theorem about the existence and uniqueness of the solutions.

**4.1.1 Theorem 1 (Picard-Lindelöf theorem).** Consider the initial value problem;

$$\begin{aligned}\frac{dx}{dt} &= f(t, x), \\ x(t_0) &= x_0.\end{aligned} \quad (4.1.1)$$

Let  $f : D \subset \mathbb{R} \times \mathbb{R}^n \rightarrow \mathbb{R}^n$  be continuous and locally Lipschitz in the variable  $x$ , for some open set  $D$ . Then for every  $(t_0, x_0) \in D$ , there exist a unique solution  $x(t)$  of Equation (4.1.1) defined on some open interval  $I$  that contains  $t_0$  (Barreira and Valls, 2012).

*Proof.* See (Barreira and Valls, 2012).

A known result from Real analysis states that if a function is  $C^1$  (i.e it is differentiable with continuous derivatives), then it is locally Lipschitz (Barreira and Valls, 2012). In the case of interest to us, the

vector field of Equation (3.2.2) is a polynomial function which means it is  $C^\infty$  and hence  $C^1$ , as a result it is locally Lipschitz. This then allows us to apply the Picard-Lindelöf theorem to conclude that the initial value problems for (3.2.2) always have a unique solution defined for  $t$  in some neighbourhood of the initial time, as we will see in Proposition 1.

**4.1.2 Proposition 1.** Solutions to the system given by Equation (3.2.2) are non-negative and bounded.

*Proof.* Consider the system defined by the Equation (3.2.2) and the positive cone of  $\mathbb{R}^5$ ,

$$\mathbb{R}^{5+} = \{(X_1, X_2, X_3, X_4, X_5) : X_k \geq 0, \forall k = 1, 2, 3, 4, 5\}.$$

Take an initial condition in  $\mathbb{R}^{5+}$  say,

$$X_1 = 0 \wedge X_k > 0, \forall k = 2, 3, 4, 5.$$

Clearly, at  $t = 0$ ,  $X_1(0) = 0, X_k(0) > 0, \forall k = 2, 3, 4, 5$ . Now from Equation (3.2.2)(-1), we have that at  $t = 0$ ,

$$\frac{dX_1(0)}{dt} = k_{-1}X_2(0)H_2 > 0.$$

Since  $X_1(0) = 0$  we can conclude from the standard calculus result about monotonicity and derivative sign of a continuously differentiable function that  $X_1(t) > 0$  for  $t > 0$ .

If  $X_1(t) > 0$ , it follows from Equation (3.2.2)(-5) that

$$\frac{dX_5}{dt} > 0 \quad \text{which implies that} \quad X_5(t) > 0, \quad t > 0.$$

Continuing to take the initial conditions in  $\mathbb{R}^{5+}$  as described above, say, for  $X_2 = 0$ , from Equation (3.2.3)(-2) we have

$$\frac{dX_2(0)}{dt} = k_1X_1(0) + k_{-2}X_3^2(0) > 0, \quad \text{therefore} \quad X_2(t) > 0, \quad t > 0.$$

Taking  $X_3 = 0$ , it follows that at  $t = 0$  from Equation (3.2.2)(-3) we have

$$\frac{dX_3(0)}{dt} = k_2X_2(0) > 0, \quad \text{therefore} \quad X_3(t) > 0, \quad t > 0.$$

Then, it follows from Equation (3.2.2)(-4) that

$$\frac{dX_4(0)}{dt} > 0, \quad \text{therefore} \quad X_4(t) > 0, \quad t > 0.$$

Therefore, it follows that if the initial condition is in  $\mathbb{R}^{5+}$ , then the solutions will be in  $\mathbb{R}^{5+}, \forall t > 0$ , meaning they never leave the cone hence they are non-negative.

The next step is to show that the solutions are bounded. We have seen that

$$X_k(t) \geq 0, \quad \forall t \geq 0, \quad \forall k \in \{1, 2, 3, 4, 5\}.$$

So, let

$$\sum_{k=1}^5 X_k(t) = X_1 + X_2 + X_3 + X_4 + X_5.$$

Then

$$\begin{aligned}
\frac{d}{dt} \sum_{k=1}^5 X_k(t) &= \frac{dX_1}{dt} + \frac{dX_2}{dt} + \frac{dX_3}{dt} + \frac{dX_4}{dt} + \frac{dX_5}{dt} \\
&= (-k_0 X_1 - k_1 X_1 + k_{-1} X_2 H_2) + (k_1 X_1 - k_{-1} X_2 H_2 + k_{-2} X_3^2 - k_2 X_2) \\
&\quad + (k_2 X_2 - k_{-2} X_3^2 - k_3 X_3^2 H_2) + (k_3 X_3^2 H_2) + (k_0 X_1) \\
&= 0.
\end{aligned} \tag{4.1.2}$$

It follows that

$$\sum_{k=1}^5 X_k(t) = \sum_{k=1}^5 X_k(0) = C_0,$$

where  $C_0$  is the constant for each initial condition. Therefore we have that

$$0 \leq X_k(t) \leq C_0 \quad \forall k \in \{1, 2, 3, 4, 5\}, \forall t \geq 0.$$

Therefore we conclude that the solutions of the system are bounded and as a consequence, they never blow up and are defined in a maximal interval containing  $[0, \infty)$ . Since we have shown that the solutions to the model are unique, in the next section we present the analysis of the equilibria of the model.

## 4.2 Equilibria

**4.2.1 Proposition 2.** The kinetic model defined by the Equation (3.2.2) has equilibria and is given by

$$(X_1^*, X_2^*, X_3^*, X_4^*, X_5^*) = (0, 0, 0, (X_4)_{eq}, (X_5)_{eq}), \tag{4.2.1}$$

where  $(X_4)_{eq} + (X_5)_{eq} = X_1(0)$ .

*Proof.* Let us assume that the system has an equilibrium point and  $H_2 \neq 0$ . Then to find the equilibria we set the right hand side of the differential equations from Equation (3.2.2) equal to zero and solve for the dependant variables. From Equation (3.2.2)(-5), we have that

$$k_0 X_1 = 0, \quad \text{then} \quad X_1 = 0.$$

Using this result in Equation (3.2.2)(-1) with the fact that  $H_2 \neq 0$ , we have that

$$k_{-1} X_2 H_2 = 0 \quad \text{hence} \quad X_2 = 0.$$

Using the result  $X_1 = 0 = X_2$  we have

$$\begin{aligned}
k_{-2} X_3^2 &= 0, \\
X_3^2 &= 0, \quad \text{hence} \quad X_3 = 0.
\end{aligned}$$

From Equation (4.1.2), it follows that

$$(X_1 + X_2 + X_3 + X_4 + X_5)(t) = \text{constant}. \tag{4.2.2}$$

Therefore from the law of mass conservation shown by Equation (4.2.2), we have that the equilibrium must satisfy

$$(X_1^*, X_2^*, X_3^*, X_4^*, X_5^*) = (0, 0, 0, (X_4)_{eq}, (X_5)_{eq}), \quad (4.2.3)$$

where  $(X_4)_{eq} + (X_5)_{eq} = X_1(0)$ , which is the result in Equation (4.2.1).

From (4.2.3) and Proposition 1 we know that the equilibria of the system in Equation (3.2.2) forms a 2-dimensional plane in the positive cone of the 5-dimensional space  $\mathbb{R}^5$ .

We have, so far shown that the model have unique solutions and also determined the nature of the model's equilibria, in the next section we look at the behaviour of the solutions to the model when we start at initial conditions close to the equilibria.

### 4.3 Linearised stability

To determine the stability of solutions, we first linearise about the equilibrium point and use the Jacobian matrix to determine the nature of the eigenvalues. Let us first consider a theorem that will help us conclude about the linearised stability of the solutions.

**4.3.1 Theorem 2 (Barreira and Valls, 2012).** The differential equation  $x' = Mx$  where  $M$  is a square matrix with eigenvalue(s)  $\lambda_i$  is;

-asymptotically stable if and only if  $M$  has only  $R_e(\lambda_i) < 0$ ,

-stable if and only if  $M$  has no  $R_e(\lambda_i) > 0$  and each eigenvalue where  $R_e(\lambda_i) = 0$  has a diagonal Jordan block, i.e has equal algebraic and geometric multiplicities, and

- unstable if and only if  $M$  has at least one  $R_e(\lambda_i) > 0$  or at least one eigenvalue with its real part zero and a non-diagonalizable Jordan block.

*Proof.* See (Barreira and Valls, 2012).

For simplicity when doing some of the analysis at this stage, let us first consider the following definitions.

**4.3.2 Definition 1.** We define  $\vec{X} = (X_1, X_2, X_3, X_4, X_5)$  as a vector containing the state variables and let  $X_{eq} \in \mathbb{R}^5$  be an equilibrium point of the system defined by Equation (3.2.2).

**4.3.3 Definition 2.** Let  $f : \mathbb{R}^5 \rightarrow \mathbb{R}^5$  be  $f = (f_1, f_2, f_3, f_4, f_5)$  where the  $f_j$  are functions on the right hand-side of the system with Equation (3.2.2). This means that;

$$\begin{aligned} f_1(\vec{X}) &= -k_0X_1 - k_1X_1 + k_{-1}X_2H_2 \\ f_2(\vec{X}) &= k_1X_1 - k_{-1}X_2H_2 + k_{-2}X_3^2 - k_2X_2 \\ f_3(\vec{X}) &= k_2X_2 - k_{-2}X_3^2 - k_3X_3^2H_2 \\ f_4(\vec{X}) &= k_3X_3^2H_2 \\ f_5(\vec{X}) &= k_0X_1 \end{aligned} \quad (4.3.1)$$

We begin by presenting a proposition that presents the linearised form of the model, i.e Equation (3.2.2).

**4.3.4 Proposition 3.** If we linearise the system of equations for the model about an equilibrium point  $X_{eq} = (X_1^*, X_2^*, X_3^*, X_4^*, X_5^*)$  given by (4.2.1), then the linearised system is given by

$$\frac{d\vec{u}}{dt} = J\vec{u}, \quad (4.3.2)$$

where

$$\vec{u} = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \end{bmatrix} \quad \text{and the Jacobian} \quad J = \begin{bmatrix} -k_0 - k_1 & k_{-1}H_2 & 0 & 0 & 0 \\ k_1 & -k_{-1}H_2 - k_2 & 0 & 0 & 0 \\ 0 & k_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ k_0 & 0 & 0 & 0 & 0 \end{bmatrix}_{X_{eq}}.$$

*Proof.* The function  $f$  given in Definition 2 is a polynomial function, hence it is  $C^\infty$ . From calculus we know that the linearisation of  $f_j(\vec{X})$  ( tangent plane approximation) about  $X_{eq}$  is given by

$$f_j(\vec{X}) \approx f_j(X_{eq}) + \partial_{X_1} f_j(X_{eq})(X_1 - X_1^*) + \partial_{X_2} f_j(X_{eq})(X_2 - X_2^*) + \partial_{X_3} f_j(X_{eq})(X_3 - X_3^*) \\ + \partial_{X_4} f_j(X_{eq})(X_4 - X_4^*) + \partial_{X_5} f_j(X_{eq})(X_5 - X_5^*).$$

We define new co-ordinates;

$$u_1 = X_1 - X_1^*, \quad u_2 = X_2 - X_2^*, \quad u_3 = X_3 - X_3^*, \quad u_4 = X_4 - X_4^*, \quad u_5 = X_5 - X_5^*.$$

Since  $X_{eq}$  is an equilibrium point, we have that  $f_j(X_{eq}) = 0$  for all the  $f_j$ 's. Taking into account that the  $X_j^*$  are constants, we have

$$\frac{du_j}{dt} = \frac{dX_j}{dt}, \quad \text{for } j=1,2,\dots,5.$$

Writing the linear system in terms of the new co-ordinates, we have

$$\begin{aligned} \frac{du_1}{dt} &= \partial_{X_1} f_1(X_{eq})u_1 + \partial_{X_2} f_1(X_{eq})u_2 + \partial_{X_3} f_1(X_{eq})u_3 + \partial_{X_4} f_1(X_{eq})u_4 + \partial_{X_5} f_1(X_{eq})u_5 \\ \frac{du_2}{dt} &= \partial_{X_1} f_2(X_{eq})u_1 + \partial_{X_2} f_2(X_{eq})u_2 + \partial_{X_3} f_2(X_{eq})u_3 + \partial_{X_4} f_2(X_{eq})u_4 + \partial_{X_5} f_2(X_{eq})u_5 \\ \frac{du_3}{dt} &= \partial_{X_1} f_3(X_{eq})u_1 + \partial_{X_2} f_3(X_{eq})u_2 + \partial_{X_3} f_3(X_{eq})u_3 + \partial_{X_4} f_3(X_{eq})u_4 + \partial_{X_5} f_3(X_{eq})u_5 \\ \frac{du_4}{dt} &= \partial_{X_1} f_4(X_{eq})u_1 + \partial_{X_2} f_4(X_{eq})u_2 + \partial_{X_3} f_4(X_{eq})u_3 + \partial_{X_4} f_4(X_{eq})u_4 + \partial_{X_5} f_4(X_{eq})u_5 \\ \frac{du_5}{dt} &= \partial_{X_1} f_5(X_{eq})u_1 + \partial_{X_2} f_5(X_{eq})u_2 + \partial_{X_3} f_5(X_{eq})u_3 + \partial_{X_4} f_5(X_{eq})u_4 + \partial_{X_5} f_5(X_{eq})u_5 \end{aligned} \quad (4.3.3)$$

Using the (4.3.1) to simplify (4.3.3) and presenting the result in matrix form, we have

$$\begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \end{bmatrix}' = \begin{bmatrix} -k_0 - k_1 & k_{-1}H_2 & 0 & 0 & 0 \\ k_1 & -k_{-1}H_2 - k_2 & 0 & 0 & 0 \\ 0 & k_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ k_0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \end{bmatrix}$$

which is the result in Equation (4.3.2).

Having linearised the model about the equilibrium point, we then present a proposition that will help us conclude about the stability of the equilibrium point.

**4.3.5 Proposition 4.** The equilibrium  $X_{eq}$  of the kinetic model defined by the system of equations from Equation (3.2.2) is stable.

*Proof.* To prove this we need to show that the Jacobian in Equation (4.3.2) has eigenvalues with non-positive real parts and those with real zero parts have equal algebraic and geometric multiplicities (see Theorem 2). To find the eigenvalues  $(\lambda_i)$ , we use the fact that they have to satisfy the characteristic equation of  $J(X_{eq})$  given by

$$\det(J(X_{eq}) - \lambda I_5) = 0,$$

where  $I_5$  is the  $5 \times 5$  identity matrix. Substituting the result in (4.3.2) above gives

$$\begin{aligned} & \begin{vmatrix} -k_0 - k_1 - \lambda & k_{-1}H_2 & 0 & 0 & 0 \\ k_1 & -k_{-1}H_2 - k_2 - \lambda & 0 & 0 & 0 \\ 0 & k_2 & -\lambda & 0 & 0 \\ 0 & 0 & 0 & -\lambda & 0 \\ k_0 & 0 & 0 & 0 & -\lambda \end{vmatrix} = 0 \\ & (-\lambda) \begin{vmatrix} -k_0 - k_1 - \lambda & k_{-1}H_2 & 0 & 0 \\ k_1 & -k_{-1}H_2 - k_2 - \lambda & 0 & 0 \\ 0 & k_2 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{vmatrix} = 0 \\ & (-\lambda)(-\lambda)(-\lambda) \begin{vmatrix} -k_0 - k_1 - \lambda & k_{-1}H_2 \\ k_1 & -k_{-1}H_2 - k_2 - \lambda \end{vmatrix} = 0 \\ & \lambda^3 ([-k_0 - k_1 - \lambda][-k_{-1}H_2 - k_2 - \lambda] - k_1 k_{-1} H_2) = 0 \\ & \lambda^5 + (k_0 + k_1 + k_2 + k_{-1}H_2)\lambda^4 + (k_0 k_2 + k_1 k_2 + k_0 k_{-1} H_2)\lambda^3 = 0. \end{aligned} \quad (4.3.4)$$

It follows that the eigenvalues are given by Equation (4.3.4), which upon solving gives

$$\lambda = 0 \quad (\text{with algebraic multiplicity of } 3) \quad (4.3.5)$$

$$\lambda_{\pm} = \frac{-(k_0 + k_1 + k_2 + k_{-1}H_2)}{2} \pm \frac{\sqrt{(k_0 + k_1 + k_2 + k_{-1}H_2)^2 - 4(k_0 k_2 + k_1 k_2 + k_0 k_{-1} H_2)}}{2} \quad (4.3.6)$$

From Equation (4.3.6), we have essentially two cases;

*Case 1* Where  $(k_0 + k_1 + k_2 + k_{-1}H_2)^2 - 4(k_0 k_2 + k_1 k_2 + k_0 k_{-1} H_2) \geq 0$ .

In this case,  $\lambda_{\pm} \in \mathbb{R}$  and clearly

$$\lambda_- < 0.$$

Now, for  $\lambda_+$ , we observe that

$$0 \leq (k_0 + k_1 + k_2 + k_{-1}H_2)^2 - 4(k_0 k_2 + k_1 k_2 + k_0 k_{-1} H_2) < (k_0 + k_1 + k_2 + k_{-1}H_2)^2,$$

and thus

$$\lambda_+ < \frac{-(k_0 + k_1 + k_2 + k_{-1}H_2) + |k_0 + k_1 + k_2 + k_{-1}H_2|}{2} = 0.$$

*Case 2* Where  $(k_0 + k_1 + k_2 + k_{-1}H_2)^2 - 4(k_0 k_2 + k_1 k_2 + k_0 k_{-1} H_2) < 0$ .

In this case the eigenvalues are complex and

$$R_e(\lambda_{\pm}) = \frac{-(k_0 + k_1 + k_2 + k_{-1}H_2)}{2} < 0.$$

From Equation (4.3.5) we have that  $\lambda = 0$  is an eigenvalue of  $J$  with algebraic multiplicity 3. To conclude whether the equilibrium is stable or not, we have to determine the geometric multiplicity of the null eigenvalue. The eigenspace associated with  $\lambda$  is the set of vectors belonging to  $E_{\lambda} = N(J - \lambda I)$ , where  $N$  is the null-space for  $J - \lambda I$  and  $I$  is an identity matrix. Since  $\lambda = 0$ , we have

$$E_0 = N(J).$$

Evaluating the null-space of  $J$  we have

$$\begin{bmatrix} -k_0 - k_1 & k_{-1}H_2 & 0 & 0 & 0 \\ k_1 & -k_{-1}H_2 - k_2 & 0 & 0 & 0 \\ 0 & k_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ k_0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} -(k_0 + k_1)v_1 + k_{-1}H_2v_2 \\ k_1v_1 - (k_{-1}H_2 + k_2)v_2 \\ k_2v_2 \\ k_0v_1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}.$$

This means

$$v_1 = v_2 = 0 \quad \text{and} \quad v_3, v_4, v_5 \quad \text{are arbitrary.}$$

Hence

$$E_0 = \{(0, 0, v_3, v_4, v_5) \in \mathbb{R}^5\}. \quad (4.3.7)$$

This means that the algebraic and geometric multiplicities of  $\lambda = 0$  are both equal to 3 hence, by *Theorem 2* we conclude that the equilibrium  $X_{eq}$  is stable.

The linear stability analysis above allow us to conclude that if we start with an initial condition  $(X_1, X_2, X_3, X_4, X_5)(0)$  sufficiently close to an equilibrium  $X_{eq}$  given by (4.2.3), then the solution of Equation (3.2.2) will stay close to that equilibrium. However, it cannot be applied to the initial condition  $(X_1(0), 0, 0, 0, 0)$  which is the one relevant from a chemistry point of view.

In order to study these cases we need a global method, i.e, a tool that does not depend on the linear approximation (about a single solution ) of the vector field of  $f$ . One such approach is provided by the theory of compartmental systems (Jacquez and Simon, 1993) that we will briefly present in the next section.

## 4.4 A brief introduction to compartmental systems

Consider the system below

$$\dot{\mathbf{m}} = \mathbf{F}\mathbf{m} + \mathbf{I}, \quad (4.4.1)$$

where  $\mathbf{m}$  is the mass of the system's components,  $\mathbf{F}$  is the coefficient matrix (which may depend on  $m$ ) and  $\mathbf{I}$  is the flow of materials into and out of the system from and to the environment. A compartment is a unit of the system's material that directly mixes with any inflowing material at all time, hence it is said to be a homogeneous entity. Let us consider Figure 4.1 which is a representative of an  $i$ th compartment of an  $n$  compartmental system.

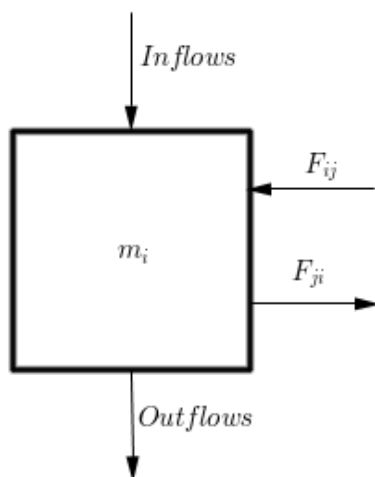


Figure 4.1: A single compartment of a compartmental system and its flows (Jacquez and Simon, 1993).

In Figure 4.1,  $m_i$  represents the mass of the  $i$ th compartment,  $F_{ij}$  is the flow of material from compartment  $j$  to  $i$  and  $F_{ji}$  is the flow from compartment  $i$  to  $j$ . The inflows and outflows are the flows into and out of the compartment respectively.

If the components  $f_{ij}$  of the coefficient matrix  $\mathbf{F}$ , satisfies the following conditions;

$$\begin{aligned}
 & - f_{ii} \leq 0, \quad \forall i, t \geq 0, \\
 & - f_{ij} \geq 0, \quad \forall i \neq j, t \geq 0, \\
 & - \sum_{i=1}^n f_{ij} = \sum_{i \neq j} f_{ij} + f_{jj} = -f_{0j} \leq 0, \quad \forall j, t \geq 0,
 \end{aligned} \tag{4.4.2}$$

then Equation (4.4.1) is said to be a compartmental system. Basically Condition (4.4.2)(-3) tells us that the sum of the entries for each column of the matrix  $\mathbf{F}$  are non positive (Jacquez and Simon, 1993). The equations of compartmental systems describe the flows amongst the compartments and they are subject to the law of conservation of mass. In cases where there are no flows, i.e  $\mathbf{I}=\mathbf{0}$ , the compartmental system is said to be closed.

We have defined what is a compartmental system, we now consider the theorem below that is associated with compartmental systems.

**4.4.1 Theorem 3 (Jacquez and Simon, 1993).** Let

$$\dot{\mathbf{X}} = \mathbf{F}(\mathbf{X}) \tag{4.4.3}$$

be a  $C^1$  differential equation which is on a subset  $S$  of  $\mathbf{R}^n$ . Suppose that  $D\mathbf{F}(\mathbf{X})$ , the Jacobian of  $\mathbf{F}$  at  $\mathbf{X}$  in  $S$ , is a compartmental matrix i.e, its elements satisfies (4.4.2). Then;



- the function  $G(\mathbf{X}) = \sum_i |F_i(\mathbf{X})|$  is a Lyapunov function for Equation (4.4.3), i.e, it is monotonically decreasing on non-constant orbits  $\mathbf{X}$  of Equation (4.4.3),
- each orbit of Equation (4.4.3) is either unbounded or tends to the set of equilibrium points.

*Proof.* See (Jacquez and Simon, 1993).

Theorem 3 provides us with a clear tool to use to determine the global stability of a system of differential equations of the form in Equation (4.4.1). Clearly the chemical system we have in Equation (3.2.2) takes the form of Equation (4.4.1) with  $\mathbf{I} = 0$ . If we are able to test if its jacobian is a compartmental matrix, then using Theorem 3 we can conclude about its stability as we will see in the next proposition.

**4.4.2 Proposition 5.** All orbits of the system given by Equation (3.2.2) tends to the set of equilibrium points, hence the equilibria are stable.

*Proof* Re-writing Equation (3.2.2) in vector form gives

$$\dot{\mathbf{X}} = \mathbf{F}(\mathbf{X}) \quad (4.4.4)$$

$$\text{where } \dot{\mathbf{X}} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \end{bmatrix}', \quad \mathbf{F}(\mathbf{X}) = \begin{bmatrix} (-k_0 - k_1)X_1 + k_{-1}H_2X_2 \\ k_1X_1 - (k_2 + k_{-1}H_2)X_2 + k_{-2}X_3^2 \\ k_2X_2 - (k_{-2} + k_3H_2)X_3^2 \\ k_3H_2X_3^2 \\ k_0X_1 \end{bmatrix}.$$

It follows from Definition 2 that the  $\mathbf{F}$  in the right side of Equation (4.4.4) is a continuously differentiable function. Proceeding the same way as in the proof of Proposition 3, the jacobian of Equation (4.4.4) is given by

$$D\mathbf{F}(\mathbf{X}) = \begin{bmatrix} -k_0 - k_1 & k_{-1}H_2 & 0 & 0 & 0 \\ k_1 & -k_2 - k_{-1}H_2 & 2k_{-2}X_3 & 0 & 0 \\ 0 & k_2 & -2k_{-2}X_3 - 2k_3H_2X_3 & 0 & 0 \\ 0 & 0 & 2k_3H_2X_3 & 0 & 0 \\ k_0 & 0 & 0 & 0 & 0 \end{bmatrix}. \quad (4.4.5)$$

To prove that the Jacobian (4.4.5) is a compartmental matrix, we need to show that it satisfies Conditions (4.4.2). Recall that the  $H_2$  and all the rate constants  $k_i$ 's are non negative as well as the  $X_i$ 's.

We start by Condition (4.4.2)(-1). So we have

$$f_{11} = -k_0 - k_1 < 0, \quad f_{22} = -k_2 - k_{-1}H_2 < 0, \quad f_{33} = -2k_{-2}X_3 - 2k_3H_2X_3 < 0, \quad f_{44} = 0, \quad f_{55} = 0.$$

Clearly all  $f_{ii} \leq 0 \quad \forall \quad i = 1, 2, \dots, 5, t \geq 0$  hence Condition 1 is satisfied.

For Condition (4.4.2)(-2) we have;

$$\begin{aligned} f_{12} &= k_{-1}H_2 > 0 \quad \text{and} \quad f_{1j} = 0 \quad \text{for } j=3,4,5, \\ f_{21} &= k_1 > 0, \quad f_{23} = 2k_{-2}X_3 > 0 \quad \text{and} \quad f_{2j} = 0 \quad \text{for } j=4,5, \\ f_{32} &= k_2 > 0 \quad \text{and} \quad f_{3j} = 0 \quad \text{for } j=1,4,5, \\ f_{43} &= 2k_3H_2X_3 > 0 \quad \text{and} \quad f_{4j} = 0 \quad \text{for } j=1,2,5, \\ f_{51} &= k_0 > 0 \quad \text{and} \quad f_{5j} = 0 \quad \text{for } j=2,3,4,5. \end{aligned}$$

Again, all  $f_{ij} \geq 0$ ,  $\forall i \neq j, t \geq 0$ , therefore Condition 2 is satisfied.

Finally for Condition (4.4.2)(-3) we need to sum along the entries of each column of  $DF(\mathbf{X})$  and determine if all the sums are non positive. Summing entries for column 1 gives

$$-k_0 - k_1 + k_1 + k_0 = 0.$$

Summing for column 2 gives

$$k_{-1}H_2 - k_2 - k_{-1}H_2 + k_2 = 0.$$

For column 3 we have

$$2k_{-2}X_3 - 2k_{-2}X_3 - 2k_3H_2X_3 + 2k_3H_2X_3 = 0.$$

For columns 4 and 5 all the entries are 0 hence their sums will be 0. We therefore have that all the sums of the entries of each column in matrix (4.4.5) are non positive. Since the matrix in (4.4.5) satisfies all the conditions in (4.4.2), we conclude that it is a compartmental matrix.

From Proposition 1, we have that the orbits of Equation (3.2.2) are bounded then from Theorem 3, we conclude that all orbits of the system tends to the set equilibrium points, which forms a 2 dimensional plane in the positive cone in the  $\mathbb{R}^5$  space, hence the equilibria are stable.

The determination of exactly which of the equilibria is the limit of the solution starting at a given initial condition  $(X_1(0), 0, 0, 0, 0)$  is a very difficult problem that does not seem to be completely understood at present. The limit point, which always satisfies

$$X_4^* + X_5^* = X_1(0),$$

depends on the values of  $k_i, H_2$ , and  $X_1(0)$  as the simulations in the next chapter illustrates.

## 5. Results

In this chapter we present the experimental results as well as simulations from the model. The simulations were done using a programming language called Julia which contains a built in package, *DifferentialEquations.jl* for the simulations and uses the Runge–Kutta fourth-order method. The experimental results were plotted using MS Excel where the equilibrium concentrations of the products are shown using bar plots. The results are presented at different ratios of hydrogen to glycerol.

### 5.1 Experimental results

To obtain the results in Figure 5.1 below, the concentrations of the products were calculated at the end of the reaction.

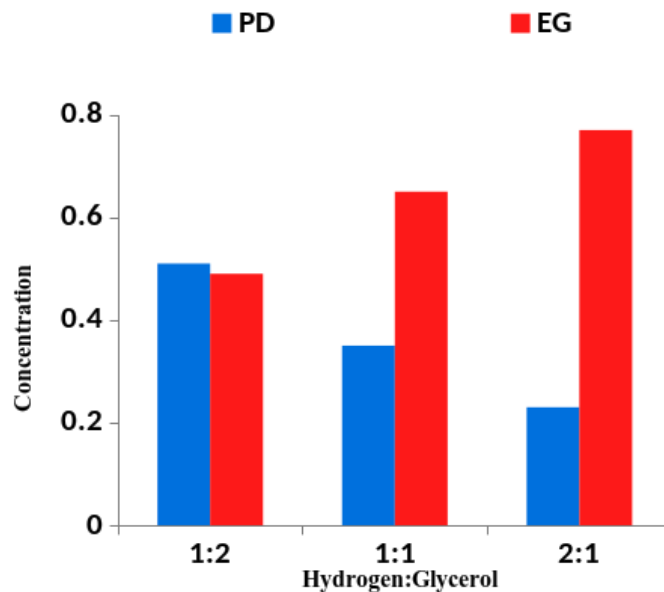


Figure 5.1: Equilibrium concentrations of EG and PD at different Hydrogen:Glycerol ratios (Shozi et al., 2017).

The experimental results showed that when there is more glycerol than hydrogen, the reaction favours the production of PD over EG. However, increasing the amount of hydrogen over that of glycerol results in the production of more EG over .

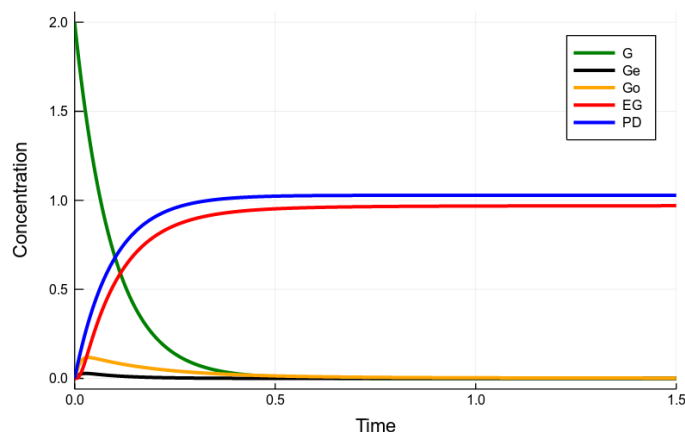
In the next section we present the simulations from the model in an attempt to compare them with the experimental results. We also present the model results on the limit points for the solutions for each case.

## 5.2 Model simulations

The simulations were done at 3 different ratios of hydrogen to glycerol and they are presented below. We start by comparing the model simulations using the given parameters in Tables 5.1, 5.2, 5.3 with the experimental results shown in Figure 5.1.

### Hydrogen:Glycerol ratio of 1:2

Figure 5.2 shows the model simulations when the amount of initial glycerol was two times more than that of hydrogen along side the actual parameter values used.



Parameter	Value Used
$k_0$	$55.0 \times 10^{-1}$
$k_1 = k_{-1}$	$0.53 \times 10^1$
$k_2 = k_{-2}$	$0.53 \times 10^3$
$k_3$	$0.53 \times 10^3$

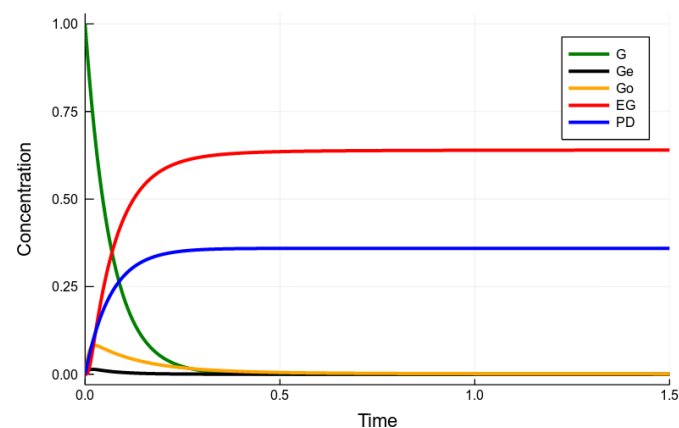
Figure 5.2: Simulation at Hydrogen:Glycerol ratio of 1:2

Table 5.1: Corresponding parameter values

The simulations from the model showed that when the initial amount of glycerol is more than that of hydrogen, and using the parameters given in Table 5.1 the reaction favours the production of the PD over the EG, just like what is in the experimental results. Also from the model, we see that the glycerol is converted slowly into the products when the hydrogen is less than the glycerol compared to Figures 5.3 and 5.4.

### Hydrogen:Glycerol ratio of 1:1

For equal amounts of initial glycerol and hydrogen, the model results obtained are shown in Figure 5.3 below alongside the parameter values used for the simulation.



Parameter	Value Used
$k_0$	$55.0 \times 10^{-1}$
$k_1 = k_{-1}$	$1.0 \times 10^1$
$k_2 = k_{-2}$	$1.0 \times 10^3$
$k_3$	$1.0 \times 10^3$

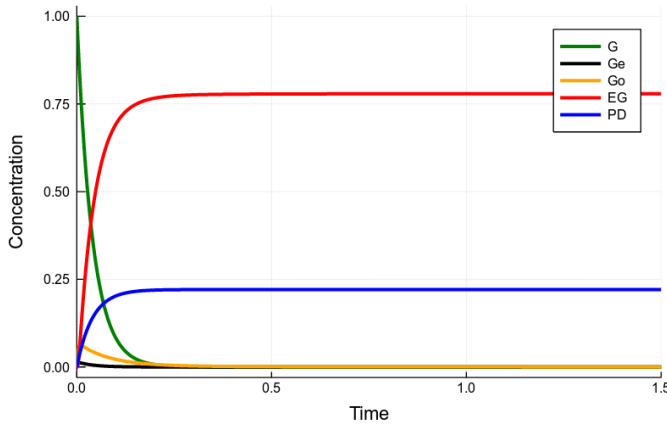
Figure 5.3: Simulation at Hydrogen:Glycerol ratio of 1:1

Table 5.2: Corresponding parameter values

When we have equal initial amounts of glycerol and hydrogen, the model predicted that more EG will be produced than PD, a result similar to the one obtained experimentally. At this point, the glycerol is converted into products faster as we can see the curve in Figure 5.3 for glycerol decays more fast than in Figure 5.2.

**Hydrogen:Glycerol ratio of 2:1**

When the hydrogen used was two times more than the initial glycerol, the model simulations obtained were as shown in Figure 5.4 below along side the parameter values used for the simulation.



Parameter	Value Used
$k_0$	$55.0 \times 10^{-1}$
$k_1 = k_{-1}$	$2.0 \times 10^1$
$k_2 = k_{-2}$	$2.0 \times 10^3$
$k_3$	$2.0 \times 10^3$

Figure 5.4: Simulation at Hydrogen:Glycerol ratio of 2:1

Table 5.3: Corresponding parameter values

The model showed that increasing the amount of hydrogen over that of glycerol still promotes the production of EG over PD as shown by the experimental results. Also, the glycerol is converted into products even much faster than the above two cases.

Having presented the model simulations, we then present the approximations of the limit points for each case as illustrated below.

**5.2.1 Limit Points** . For the different ratios of hydrogen to glycerol the limit points were computed by  $X_i^* = \lim_{t \rightarrow \infty} X_i(t)$ , for  $i = 1, 2, 3, 4, 5$ . These were well approximated by the values of  $X_i$ 's at large values of  $t$ , say  $t^*$ , depending on the simulation.

Table 5.4 below shows the limit points, i.e  $(X_1^*, X_2^*, X_3^*, X_4^*, X_5^*)$  from the simulations at the different ratios of hydrogen to glycerol, correct to 2 decimal places.

H : G	$X_1(0)$	Limit Point	$X_4^* + X_5^*$
1 : 2	2.00	(0.00, 0.00, 0.00, 0.97, 1.03)	2.00
1 : 1	1.00	(0.00, 0.00, 0.00, 0.64, 0.36)	1.00
2 : 1	1.00	(0.00, 0.00, 0.00, 0.78, 0.22)	1.00

Table 5.4: Limit points at different H:G ratios at  $t^* = 1.5$

Having presented the model simulations and compared them with the experimental results, we then investigate the effects of the constants  $k_1$  and  $k_{-1}$  by fixing the the other constants and the ratio of hydrogen to glycerol at 1:1.

**Effects of  $k_1, k_{-1}$  to the production of EG and 1,2-PD**

When the ratio of hydrogen to glycerol was fixed at 1:1 as well as  $k_0, k_2, k_{-2}, k_3$  and only varying  $k_1$  and  $k_{-1}$  results were obtained and are given in the following figures.

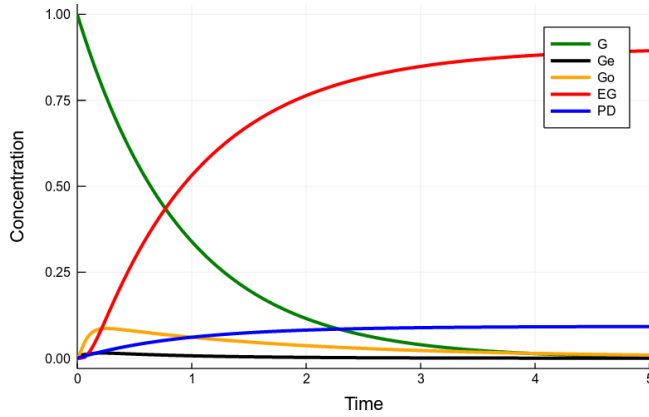


Figure 5.5: Simulation at Hydrogen:Glycerol ratio of 1:1

Parameter	Value Used
$k_0$	$1.0 \times 10^{-1}$
$k_1 = k_{-1}$	1.0
$k_2 = k_{-2}$	$1.0 \times 10^2$
$k_3$	$1.0 \times 10^2$

Table 5.5: Corresponding parameter values

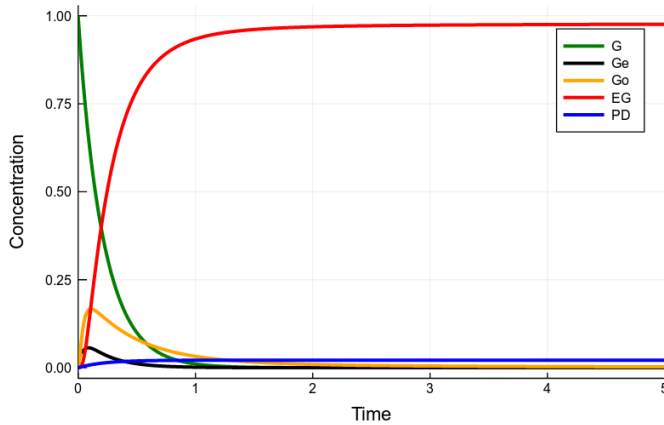


Figure 5.6: Simulation at Hydrogen:Glycerol ratio of 1:1

Parameter	Value Used
$k_0$	$1.0 \times 10^{-1}$
$k_1 = k_{-1}$	10.0
$k_2 = k_{-2}$	$1.0 \times 10^2$
$k_3$	$1.0 \times 10^2$

Table 5.6: Corresponding parameter values

The results shows that increasing the values of  $k_1$  and  $k_{-1}$  yields to an increases the amount of EG produced and the reaction reaches equilibrium faster as it seen the the Figures 5.5 and 5.6. Limit points were also approximated like in the above way (see Section 5.2.1) and they are presented in Table 5.7 below, correct to 2 decimal places.

Figure	$X_1(0)$	Limit Point	$X_4^* + X_5^*$
Fig 5.5	1.00	(0.00, 0.00, 0.00, 0.91, 0.09)	1.00
Fig 5.6	1.00	(0.00, 0.00, 0.00, 0.99, 0.01)	1.00

Table 5.7: Limit points when varying  $k_1, k_{-1}$  and fixing the other parameters at  $t^* = 5.0$

We have presented the findings from the experiment and the model simulations, in the next chapter we then proceed by presenting the discussion of both the mathematical results and the simulations.

## 6. Discussion and Conclusion

In this chapter we present the analysis of the mathematical results and model simulations, conclusions as well as future work. We start by presenting the discussion of the results obtained from the mathematical analysis of the model.

### 6.1 Mathematical results analysis

The kinetic model consists of a 5-dimensional system of autonomous nonlinear ordinary differential equations for the evolution of the concentrations  $X_j(t)$ ,  $j = 1, \dots, 5$  of the chemical species taking part in the chemical reaction scheme. The mathematical investigations of the system showed that all its solutions converge to some limit point as  $t \rightarrow +\infty$ , which may depend on the initial condition. This is so because we have shown rigorously that all solutions to the model with non-negative initial data are bounded and positive, hence we expect that the trajectories converge to a stable bounded attractor set. Due to the special structure of the vector field defining the model (a compartmental type system) this attractor can only be made of equilibria, as shown in Proposition 5.

From Proposition 2, it can also be pointed out that the solutions of the model are in the part of a two dimensional plane lying inside the positive cone in the  $\mathbb{R}^5$  space. We also proved that the differential equations satisfy the conservation of mass law (Proposition 1) from which it follows that the solution converges to limit points as  $t \rightarrow +\infty$ , (that depend on the initial conditions and values of  $k_i$ ) all satisfying  $X_4^* + X_5^* = X_1(0)$ . This convergence, that is generally valid for all non-negative initial data due to the compartmental nature of the system (see above), was also proved for initial conditions close to the equilibria. This was done using the linearisation method, since the eigenvalues of the linearisation matrices turn out to have non-negative real parts and those with zero real parts are simple (i.e.: have equal algebraic and geometric multiplicities), as we proved in Proposition 4.

We then look at the discussion of the simulations from the model.

### 6.2 Model simulation analysis

The model and experimental results have almost similar outcomes in all the 3 different ratios of hydrogen to glycerol. From Figure 5.2 where we have initial glycerol concentration two times more than hydrogen, the model results showed that more PD is produced over EG. This is because, according to Shozi et al. (2017) the Cu-Re/ZnO catalyst used have acidic sites which favours the removal of a water molecule over that of hydrogen, hence more PD is produced over EG. From Figures 5.3 and 5.4, an increase in the hydrogen to glycerol ratio led to an increase in the production of EG over PD. This can be due to the further hydrogenolysis of the PD into EG and other products, as reported in the report by Shozi et al. (2017).

The model results also showed that an increase in the hydrogen to glycerol ratio resulted in the increase in the conversion of glycerol into the products. This is likely caused by the increase in the catalyst's activity in the presence of hydrogen, which promotes mostly the removal of hydrogen gas from glycerol over the water molecule. Likewise, the results showed that increasing the amount of hydrogen over that of glycerol does not necessarily bring great change in the amount of EG produced since their equilibrium

concentrations do not differ much. If increasing the amount of hydrogen does not bring much increase in EG production, it means that the hydrogenolysis process is cost-effective, since the production of hydrogen is very costly ([ENERGY.GOV](http://ENERGY.GOV)).

When we fixed the ratio of hydrogen to glycerol at 1:1 as well as the other constants while varying only  $k_1, k_{-1}$ , the model simulation showed that an increase in the value of  $k_1, k_{-1}$  results in an increase in the production of EG, as shown in Figure 5.6. This is because, from system (3.2.1) we see that an increase in these constants means more glycolaldehyde will be formed which consequently means more glyceraldehyde is produced hence the increase in the EG formed. At higher  $k_1, k_{-1}$ , the reaction reaches equilibrium faster than at lower values as it is shown by Figures 5.5 and 5.6. This might be due to that the intermediates are produced at a higher rate and quickly utilized into products as shown by Figure 5.6, we have more glycolaldehyde produced and quickly levels to 0 compared to Figure 5.5.

### 6.3 Conclusion

The reaction for the hydrogenolysis of glycerol can be modelled using a system of ordinary differential equations and the model simulations were aligned with how the reaction proceeds in the chemistry point of view. All solutions of the model converge to some stable limit point in a 2 dimensional plane of a positive cone in the  $\mathbb{R}^5$  space, and they depend on the values of  $k_i$  and hydrogen to glycerol ratio used. However, finding the exact limit point to which the solutions converge to, is a problem that is not fully understood at the moment, possibly due to the fact that our model is non-linear, hence other mathematical tools needs to be used.

### 6.4 Future work

The work reported here is based on a specific chemical mechanism modelling the hydrogenolysis of glycerol published in the literature. Other models have also been proposed in the literature and it would be interesting to study those ones using the tools of mathematical analysis and simulations so that comparison with experimental results can lead to a better understanding of this important complicated catalytic mechanism that is, at present, not thoroughly understood. In fact, it is recognized that even the model studied here needs some revision since the experimental molar ratio of produced ethylene glycol:methanol is about 4:1 and not 1:1 as the kinetic scheme under consideration predicts.

Notwithstanding the concrete model to be considered in the future, the tools used in this work (mathematical analysis based on qualitative analysis tools and simulations supported by numerical solutions of ODE) are bound to be crucial in that process. A deeper understanding might also require other mathematical tools that have not been studied or used here, such as methods from asymptotic analysis, and others.



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