

Influence of number of catalytic sites in 1,3-butadiene solution polymerizations catalysed by titanium tetrachloride

Francisco R. L. Farias¹ | Mateus K. Vasconcelos*² | Amanda L. T. Brandão¹

¹Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil

²Programa de Engenharia Química/COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

Correspondence

*Corresponding Mateus K. Vasconcelos, Corresponding address.
Email: mkv@eq.ufrj.br

Abstract

The synthetic rubber industry is of great importance and it is present in the daily life of world society. BR (butadiene rubber or polybutadiene) is one of the most used polymers in this field, mainly in tire production. Therefore, the control of operational conditions and final properties of the polymer formed are important points to be studied as they are a challenge for the industry. Thus, the present work focus in simulate the batch polymerization of polybutadiene using the *Aspen Plus* software, where 1,3-butadiene, titanium tetrachloride, triethylaluminium and hexane were used as monomer, catalyst, co-catalyst and solvent, respectively. Four cases were simulated changing the number of catalyst sites in order to predict and compare the final properties of polybutadiene resins including the average molecular weights, the molecular weight distribution and the evolution of operation conditions that are used at plant to monitor the course of the reaction like the reaction temperature and pressure.

KEYWORDS

Aspen Plus, Molecular weight distribution, Polybutadiene, Simulation.

1 | INTRODUCTION

Rubber is a kind of polymer that can be natural or artificial and it's an important material used in the tire industry, footwear, automotive accessories, health related products, among others. Natural rubber is obtained from latex, which is produced in many tropical plant species. Almost all the world's natural rubber production comes from the rubber tree (*Hevea brasiliensis*) latex extraction, although many tropical plant species produce this material [1].

Natural rubber has some properties that make their use difficult. For example, in cold temperatures it becomes hard and brittle, while in higher temperatures it becomes soft and sticky. Due to this fact, Charles Goodyear started to research in 1839 the process called vulcanization. In this process, sulfur was added to the polymer causing its double bonds to

1 break and forms sulfur bridges that bind the side chains, decreasing hysteresis, reducing
 2 permanent deformation and increasing elasticity [2].
 3 From then on, studies began to be carried out on the addition polymerization reactions of dienic
 4 compounds, producing many types of synthetic rubbers. Depending on the type of monomer
 5 used to make the polymer, rubbers with different properties can be achieved.
 6 The object of this study is the simulation of polymerization of 1,3-butadiene (the structure of
 7 the monomer can be seen in Figure 1), one of the most used elastomers on the rubber industry.
 8 Also called simply butadiene rubber (BR), it is predominantly based on cis-1,4 polybutadiene
 9 and its synthesis require a catalyst usually based on a transition metal, specially the lanthanide's
 10 metals. In Table 1, it can be observed the different metals used in catalysts for performing
 11 polybutadiene and its respective microstructure. The structure of the polymer obtained from
 12 1,3-butadiene indicates the addition occurs preferably in the -1,4 positions. Notably, the carbon
 13 chain still has a double bond. Although the isomer *trans* the most stable, when catalysts based
 14 on neodymium or titanium are used, the polymer chain tends to be formed by *cis* isomers [3].
 15 **Table 1** Polybutadiene's distribution microstructures with different catalysts [4].

| Microstructure | | | |
|----------------|---------------------|-----------------------|---------------|
| Metal | 1,4- <i>cis</i> (%) | 1,4- <i>trans</i> (%) | 1,2-vinyl (%) |
| Neodymium | 98 | 1 | 1 |
| Cobalt | 96 | 2 | 2 |
| Titanium | 93 | 3 | 4 |
| Nickel | 96 | 3 | 1 |

16 The polymer has important characteristics that directly influence the properties of the final
 17 product such as melting temperature, crystallinity, malleability and flexibility [5]. One of these
 18 properties is the number-average molecular weight (M_n) and weight-average molecular weight
 19 (M_w). The first one is calculated by adding the molar masses of all chains generated throughout
 20 the process and dividing it by the total number of chains. The latter is calculated in a similar
 21 way, the focus, however, is found in the mass of the polymeric chains themselves, which makes
 22 the molar mass of each fraction contribute in a weighted way to the result.

$$M_n = \frac{\sum n_i \cdot M_i}{\sum n_i} \quad (1)$$

$$M_w = \frac{\sum n_i \cdot M_i^2}{\sum n_i \cdot M_i} \quad (2)$$

23 M_i – Molar mass of the chain

24 n_i – Number of molecules with mass M_i

25 Another important property is the dispersity that indicates the relationship between M_n and
 26 M_w . The more varied the sizes of the molecules, the greater is the dispersity value (which is
 27 always greater than 1). In the other hand, when chain sizes are close, the polydispersity is
 28 approximately 1.

$$PDI = \frac{M_w}{M_n} \quad (3)$$

29 Polybutadiene fills about 25% of the world rubber market. It can be obtained in different ways,
 30 which differ in terms of molecular microstructure, average molar masses, molar mass
 31 distributions, degree of branching, types of branching and functionalization of terminal groups
 32 [6]. It can be obtained through different types of catalysts, and free radical, cationic, anionic or
 33 coordination initiators can be used [7].

34 The high-*cis* polybutadiene is catalytically produced by Ziegler-Natta (ZN) catalysts. Among
 35 the ZN, cobalt, nickel, titanium and neodymium-based catalysts are the most employed.

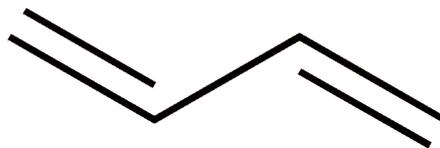


Figure 1 Molecular structure of 1,3-butadiene.

BR is used in four major areas: tire manufacturing (70%); impact alteration of thermoplastics (25%) such as high impact polystyrene (HIPS) and acrylonitrile butadiene styrene terpolymer, more commonly known as ABS; and everyday products like shoe soles and golf balls (5%) [4]. As there is a high demand for improvements of the mechanical properties of rubbers used by the tire industry, the production of high-cis polybutadiene has been the subject of several scientific studies in recent years.

Proß et al. (1993) presented a mathematical model for 1,3-butadiene polymerizations with a neodymium-based catalyst and were able to predict the MWD of the final product, the evolution of 1,3-butadiene concentrations and the dependence of the reaction rate constant on the Cl/Nd molar ratio. The authors showed that distinct catalytic systems presented distinct kinetic constants and produced rubbers with distinct properties [8].

Ling et al. (2000) proposed a Monte Carlo procedure to simulate the gas phase polymerization of 1,3-butadiene and were able to predict the MWD of the obtained products [9].

Aminova et al. (2002) developed a mathematical model to describe 1,3-butadiene polymerizations using a cobalt-based catalyst. The author's proposed model was able to simulate M_n and M_w , branching factors and sedimentation-average degrees of polymerization. It was observed the occurrence of branching reactions, chain transfer to polymer, and chain cross-linking. In another work, Aminova et al. improved the same model in order to describe a continuous process and used the model to simulate the average molecular weights of the obtained products [10] [11].

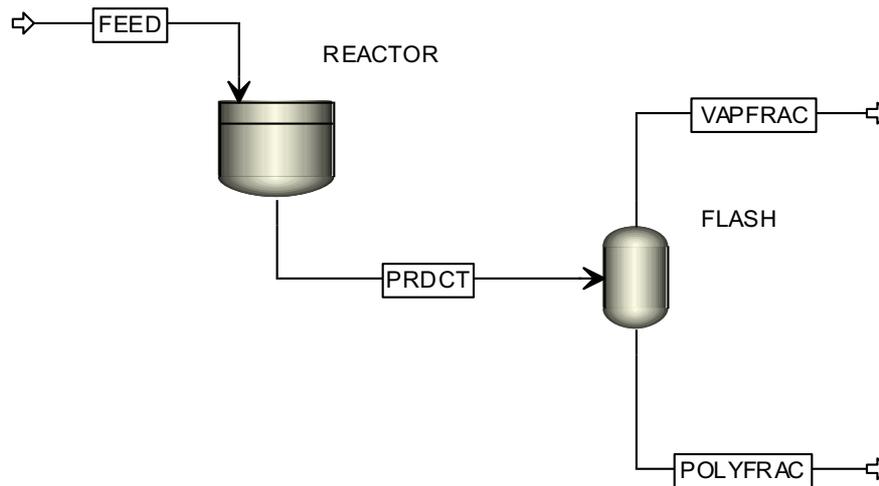
Manuiko et al. (2010) proposed a model for 1,3-butadiene solution polymerizations that considers the presence of two types of active sites in the system and the presence of hexachlorop-xylene as a chlorinating agent. Particularly, their model was able to calculate average molecular weights and branching frequencies [12].

Vasconcelos et al. (2019) developed a mathematical model for the polymerization of 1,3-butadiene using neodymium versatate as a catalyst. The model, in addition to being able to predict final properties of the polybutadiene polymer as average molecular weights and cis-content, was also able to predict the evolution of operation conditions that are used at plant site to monitor the course of the reaction like temperature and pressure [13].

As far as we have knowledge, given the described scenario, there are not many theoretical studies on the number of active catalytic sites in polymerization and their influence on the polymer molar mass distribution profile, as well as temperature and pressure profiles during the process. Thus, the objective of this work is to evaluate this influence by comparing such profiles using Aspen Plus 10 software considering the proposed kinetic mechanism that includes initiation, chain propagation, and monomer transfer steps.

2 | MATERIAL AND METHODS

The selected methodology for simulating polybutadiene polymerization is based on that described in Aspen Plus Chemical Engineering Applications for the process of forming HDPE. Choosing "Polymers with Met - C_bar_hr Units" as the thermodynamic package and "POLYNRTL" as the numerical method package, the polymerization process was simulated using a batch reactor and a flash column as shown in Figure 2.



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Figure 2 Main Flowsheet of the polybutadiene polymerization process. After choosing the thermodynamic and numerical method packages, it was added the reaction components of the process listed in Table 2.

Table 2 Components added in the simulation.

| Component | Molecular Formula | Function in process |
|------------------------|--|-------------------------|
| N-hexane | C ₆ H ₁₄ | Reaction solvent |
| 1,3-butadiene | C ₄ H ₆ | Monomer |
| Polybutadiene | (C ₄ H ₆) _n | Polymer |
| Butadiene R-1 | C ₄ H ₆ -R | Segment |
| Titanium tetrachloride | TiCl ₄ | Catalyst |
| Triethylaluminium | (C ₂ H ₅) ₃ Al | Cocatalyst |
| Nitrogen gas | N ₂ | Inert gas to pressurize |

6 The component Butadiene-R1 must be added to the simulation. It corresponds to activated
 7 monomer (Figure 3). Aspen plus has 2 different kinds of activated monomers, Butadiene R-1,
 8 which corresponds to the cis activated monomer, and Butadiene R-2, which corresponds to
 9 trans.



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Figure 3 Molecular structure of Butadiene R-1.

As seen in the literature, it is known that polybutadiene has essentially linear structure and high cis content (greater than 90%) when the used catalyst is based on titanium [6]. Therefore, it was decided to disregard the trans monomer during the simulation. The kinetic mechanism considers the following steps described in Equations (3) to (5).

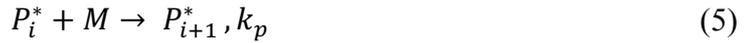
- Initiation step

$$M + Cat^* \rightarrow P_1^*(cis), k_i \quad (3)$$

- Propagation step

$$P_i^* + M \rightarrow P_{i+1}^*, k_p \quad (4)$$

- Transfer to monomer Step



The values of kinetic rate constants (k_i, k_p, k_{tm}) and activation energy were taken from the study of Vasconcelos (2019) [13], where an estimation of parameters was made from experimental data. These parameters and used for the simulation considering just one catalytic site. For the simulation considering two, three and four catalytic sites, these values were estimated in order to obtain the molar mass distribution as well M_w and M_n of polymers characteristic of the industry. All the above-mentioned constants can be found in Table 3.

Table 3 Kinect rate constants used for simulations.

| Number of sites | k_i (1/s) | k_p (1/s) | k_{tm} (1/s) |
|-----------------|---------------------------|---------------------------|--------------------------|
| 1 | 1 – 1.74x10 ⁻¹ | 1 – 2.29x10 ¹⁵ | 1 – 5.5x10 ¹³ |
| 2 | 1 – 1.74x10 ⁻¹ | 1 – 2.29x10 ¹⁵ | 1 – 5.5x10 ¹³ |
| | 2 – 2.61x10 ⁻² | 2 – 1.02x10 ¹⁶ | 2 – 5.5x10 ¹³ |
| 3 | 1 – 1.74x10 ⁻¹ | 1 – 2.29x10 ¹⁵ | 1 – 5.5x10 ¹³ |
| | 2 – 2.61x10 ⁻² | 2 – 1.02x10 ¹⁶ | 2 – 5.5x10 ¹³ |
| | 3 – 1.74x10 ⁻¹ | 3 – 6.84x10 ¹⁵ | 3 – 5.5x10 ¹³ |
| 4 | 1 – 1.74x10 ⁻¹ | 1 – 2.29x10 ¹⁵ | 1 – 5.5x10 ¹³ |
| | 2 – 2.61x10 ⁻¹ | 2 – 2.75x10 ¹⁵ | 2 – 5.5x10 ¹³ |
| | 3 – 1.74x10 ⁻¹ | 3 – 8.01x10 ¹⁵ | 3 – 5.5x10 ¹³ |
| | 4 – 5.79x10 ⁻³ | 4 – 6.41x10 ¹⁵ | 4 – 5.5x10 ¹³ |

Values of energy of activation were 88.09 kJ/mol for all propagation steps and 96.405 kJ/mol for all transfer to monomer steps.

The supply current of the reactor for all cases entered at 70°C and pressure of 2.66 bar. The molar flow is 3.88 mol/hr and the molar fraction of each component is shown in Table 4.

Table 4 Supply current of the batch reactor.

| Component | Molar Fraction |
|------------------------|-----------------------|
| 1,3 – Butadiene | 1.30x10 ⁻¹ |
| Titanium tetrachloride | 4.85x10 ⁻⁵ |
| Triethylaluminium | 8.92x10 ⁻⁵ |
| Nitrogen gas | 3.86x10 ⁻² |
| N-Hexane | 8.31x10 ⁻¹ |

The reactor used is a batch reactor with volume equal to 10L and constant thermal fluid temperature operating at 70°C with heat transfer coefficient of 2.19x10⁻³ kJ/(s.m².K). The chosen operating time was 2 hours.

The flash tower following the batch reactor was responsible to separate the polymer fraction to the vapor fraction as seen in Figure 2.

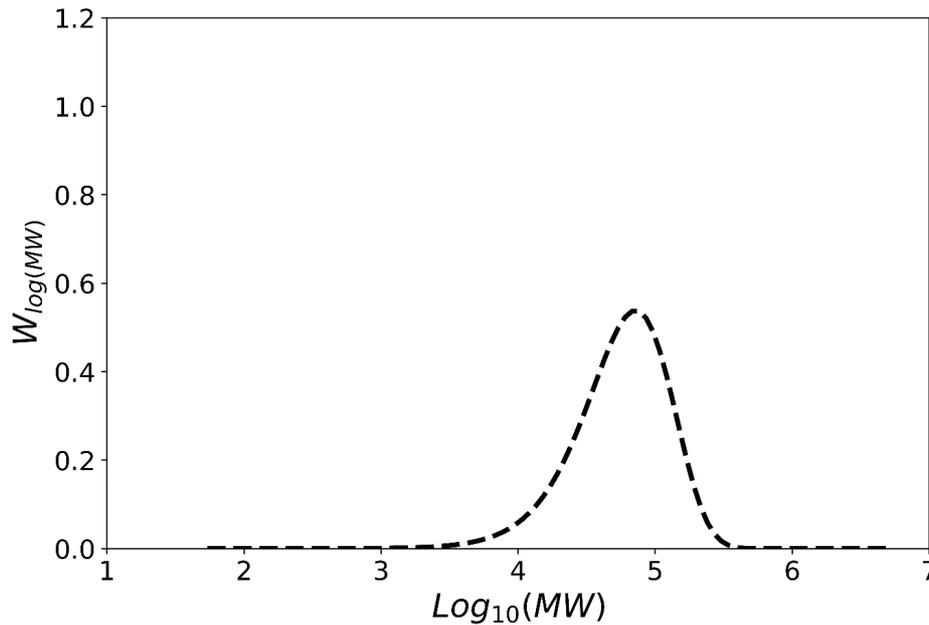
3 | RESULTS AND DISCUSSION

For all cases that will be described in this work, Aspen Plus generated the result data of mass distribution, temperature profile and pressure profile. This data was exported and treated in order to generate the plots of all the graphs that will be presented below.

For the simulation, it was generated four programs considering 1, 2, 3 and 4 catalytic sites. The kinetic rate constants of each case were selected as reported in Table 3. All cases have different results of mass distribution of polybutadiene as expected.

In cases 2, 3 and 4, the mass distribution's graphs show the curve of the composite generated and the curves below indicates the mass distribution of each catalytic site. For case 1, there is

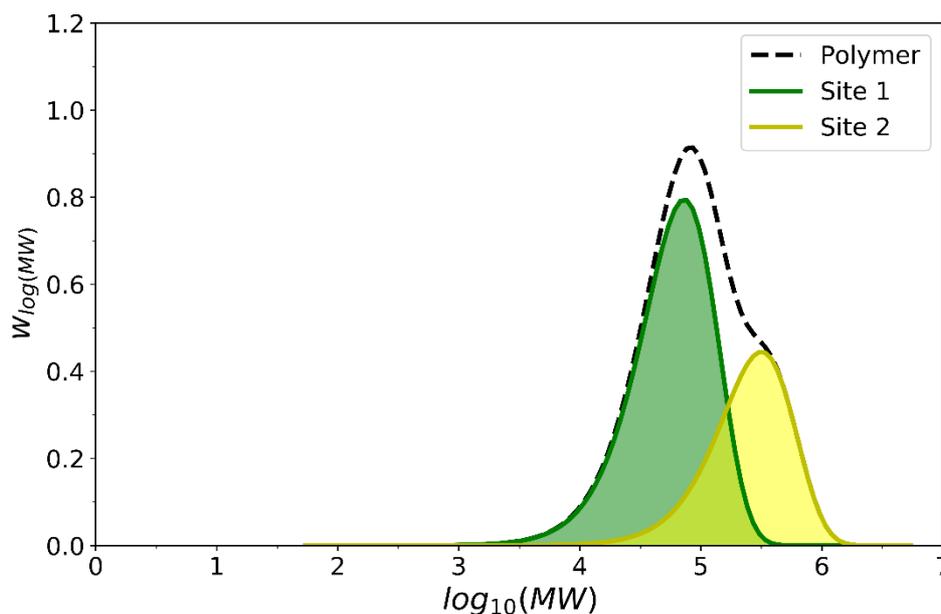
1 only one curve because there is just one catalytic site. Thus, the curve of catalytic site matches
2 with the curve of polymer. The data was treated and normalized to be presented in this work.



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4 **Figure 4** Mass distribution of polybutadiene considering only one catalytic site.

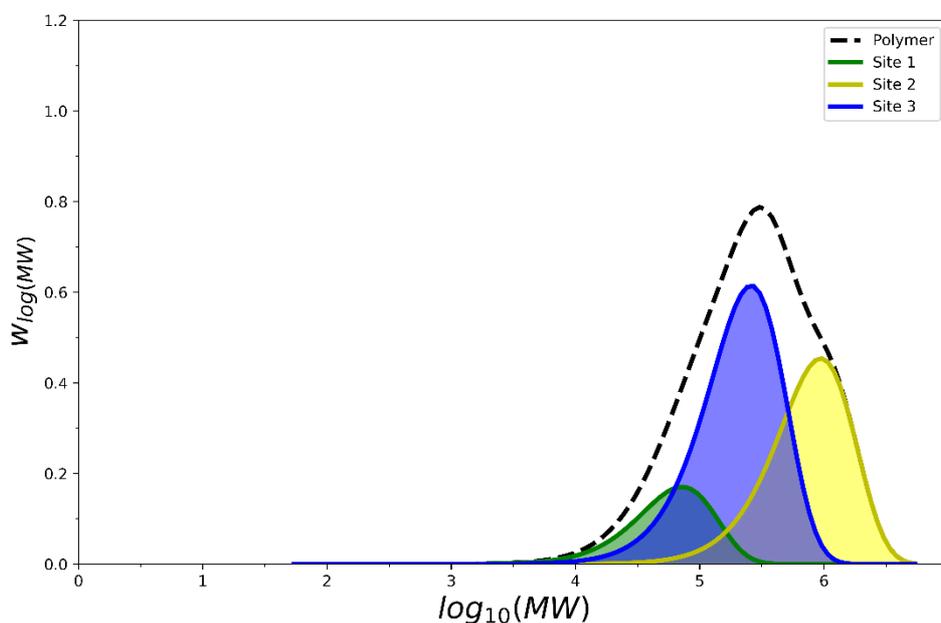
5
6 It can be seen in Figure 4 that the molar mass distribution considering only a single catalytic
7 site did not present bimodality, as expected, since the presence of only one active center
8 generates only a group of polymers following reactions with fixed kinetic constants. In
9 addition, a polydispersity index of 2.02 is observed, something very similar to a step-growth
10 polymerization process following the Flory distribution, which is expected for a catalyst with
11 only one active center [14].

12 The average molar masses are of the order of 3.61×10^4 and 7.31×10^4 for M_n and M_w ,
13 respectively, which are considered low average molar masses considering a polymerization
14 process in 1,3-butadiene solution [13][15]. In Figure 5, the process simulation can be seen
15 considering two active centres.



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17 **Figure 5** Mass distribution of polybutadiene considering two catalytic sites.

1 Comparing Figures 4 and 5, it is noted that Figure 5 presents a bimodality, while Figure 4 does
2 not. This is expected, since the presence of two active centers with different kinetic constants
3 generates polymer chains with different growths, which leads to the widening of the
4 distribution and the appearance of bimodality. This bimodality can be seen in the polydispersity
5 index, which jumped from 2 to 3.25 due to the presence of another active center. The
6 preparation of the catalyst strongly influences the presence of the active centers, since the
7 choice of reagents, the preparation time, the preparation method, the reaction temperature, the
8 storage temperature and the order of the reagents determines the formation of the active centers
9 of the catalyst [16] [17].
10 In addition, when comparing the average molar masses of the simulation with one active centre
11 with that with two active centres, an increase in the average molar masses is observed, mainly
12 in the weight-average molecular weight, which greatly increases the polydispersity index. This
13 increase is still not very significant in the general context of polybutadiene, because of that, a
14 further simulation was carried out now with three active sites, which is shown in Figure 6.



15
16 **Figure 6** Mass distribution of polybutadiene considering three catalytic sites.
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18 Now comparing Figures 5 and 6, it can be seen that bimodality remains present regardless of
19 having more active centres. Again, there is an increase in the expressive polydispersity index
20 to 4.13 indicating that the increase in the number of active centres is directly linked to the
21 widening of the molar mass distribution. Regarding the average molar masses, M_n and M_w
22 increased significantly compared to simulations with one and two active centers, where the
23 average molar masses are in the order of 10^5 . Finally, for comparison purposes, the simulation
24 with four active centres that are shown in Figure 7.

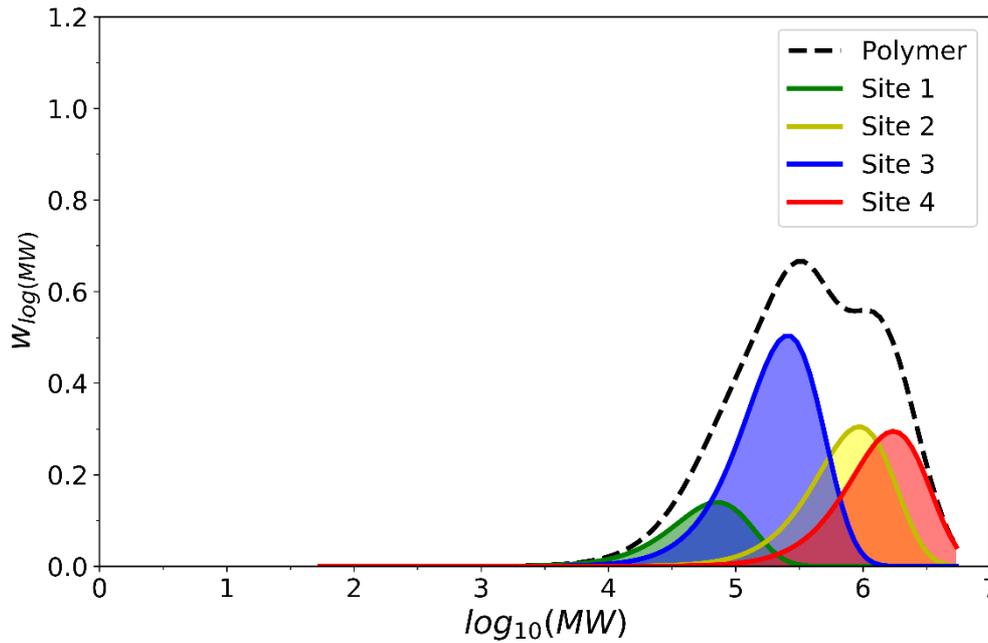


Figure 7 Mass distribution of polybutadiene considering four catalytic sites.

Comparing Figure 7 with the others, it is observed that the distribution of molar masses is significantly wider than the others, that is, the polydispersity index presented by the simulation with four active sites is the highest among the simulations and the closest to found in the literature (MÉNDEZ-HERNÁNDEZ, 2016; VASCONCELOS, 2019). The distribution still presents bimodality and the average molar masses are even greater following the trend that the more active centers, the greater the average molar masses.

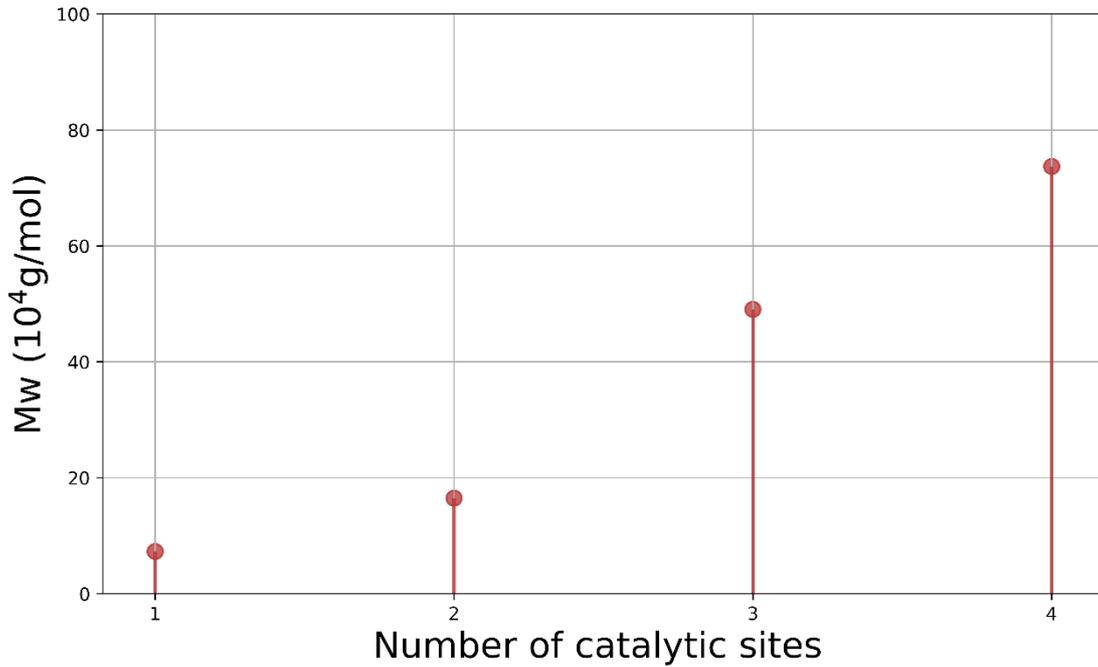
It can be seen that all curves have a Gaussian model. The curves that correspond to each site individually show unimodality. As a further catalytic site is increased, bimodality is inserted in the polymer distribution curve. It can be seen that in case 1, we have only one unimodal Gaussian curve, whereas for all other cases this bimodality is generated.

All the average molar masses and polydispersity index for all the four simulations are presented in Table 5.

Table 5 Results of M_n , M_w and PDI generated in all cases.

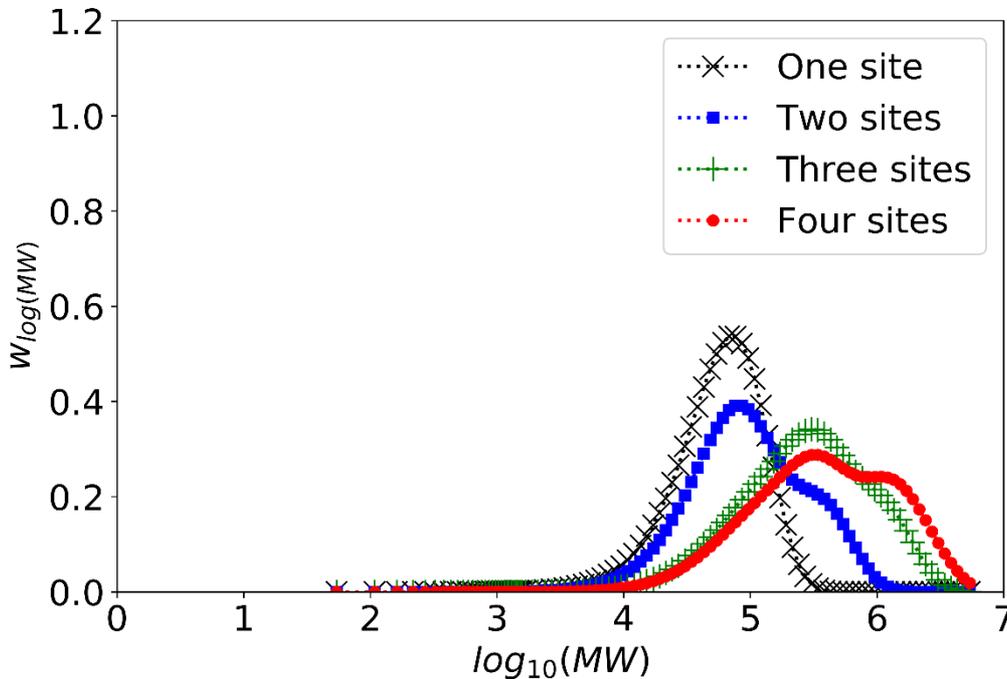
| Number of sites | $M_n \times 10^4$ (g/mol) | $M_w \times 10^4$ (g/mol) | PDI |
|-----------------|---------------------------|---------------------------|------|
| 1 | 3.61 | 7.31 | 2.02 |
| 2 | 5.08 | 16.48 | 3.25 |
| 3 | 11.88 | 49.07 | 4.13 |
| 4 | 14.06 | 73.72 | 5.24 |

In Figure 8 it can be visually seen the significant increase of M_w when we increase the number of active sites, showing the correlation that exists between the formation of more chains with the largest amount of active sites.



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Figure 8 M_w values according to the number of sites.

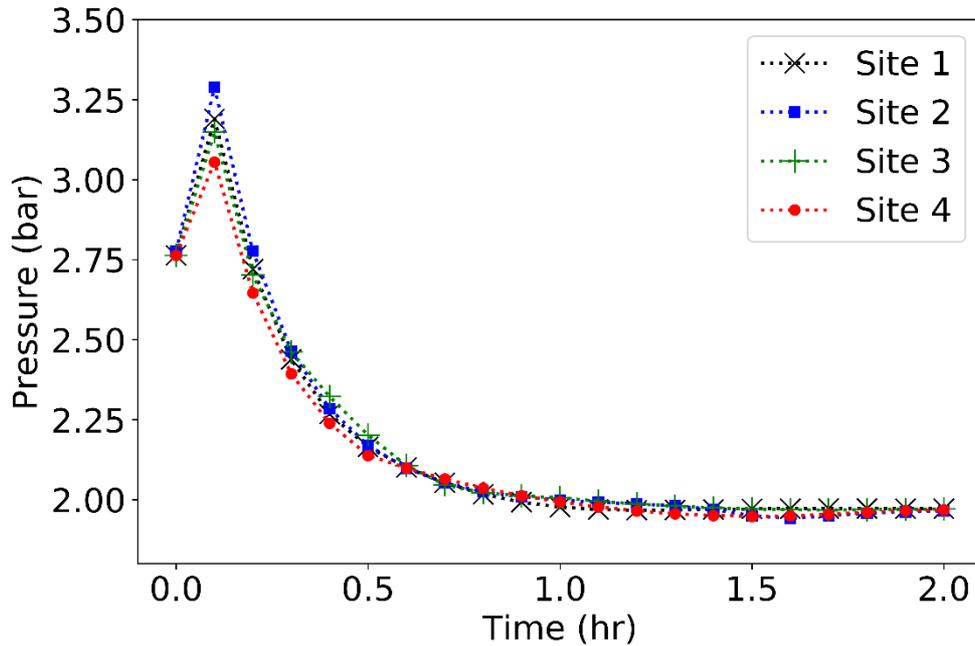
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The graph in Figure 9 was generated in order to superimpose the composite curves generated in all cases. As can be seen, the increase of number of catalytic sites shift the curves to the right. Besides that, it can be noted the difference between the width of each curve. Curve 1 has a higher peak height and a smaller width than curve 2, this in turn has a larger peak and less width than curve 3 and so on.



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Figure 9 Mass distribution of polybutadiene comparing all cases.

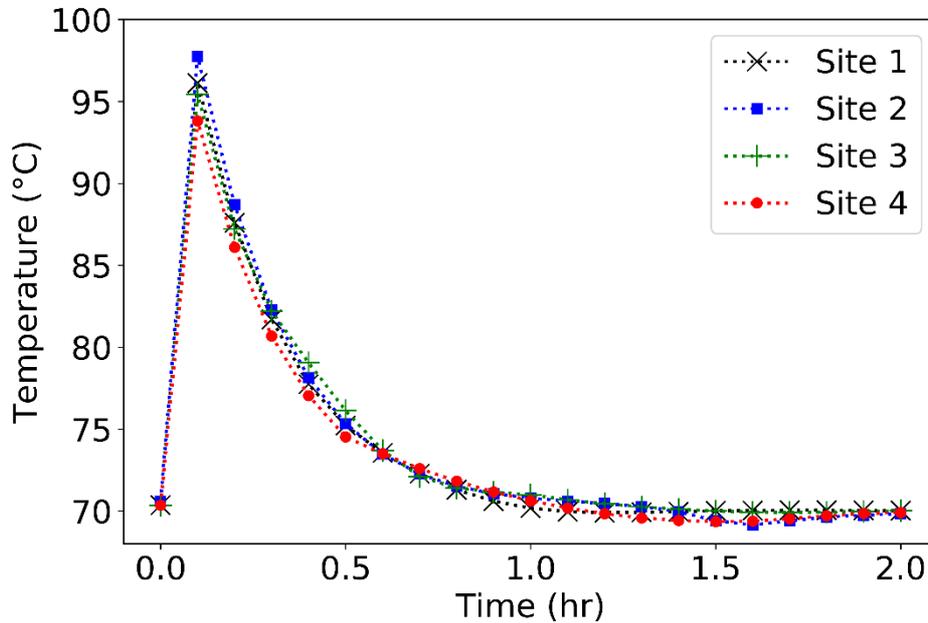
The pressure profiles for all cases were very similar with practically overlapping points. It can be noted that there were pressure peaks at the beginning of the process in the reactor, reaching values between 3.0 and 3.3 bar. However, the pressure stabilized as the reaction proceeded

1 until the initial pressure of 2 bar was reached. It was also possible to see that the pressure profile
2 considering 2 active sites had the highest peak pressure and that the profile considering 4 sites
3 obtained the lowest peak pressure as can be seen in the Figure 10.



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5 **Figure 10** Pressure profile comparing all cases.

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7 The pressure profiles obtained were considered appropriate, because they coincide with the
8 profiles obtained by Vasconcelos (2019) for both the data predicted by the model and the
9 experimental data [13]. The temperature profiles can be seen in Figure 11.



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11 **Figure 11** Temperature profile comparing all cases.

12 Temperature profiles were also obtained, and, like the pressure profiles, the curves obtained
13 for all cases showed extreme similarity with practically overlapping points. There were
14 temperature peaks between 94 and 98°C at the beginning of the reaction, but over time this
15 temperature stabilized reaching the initial value of 70°C. The highest peak presented was that
16 representing case 2 and the lowest peak represents case 4.

1 Observing the pressure and temperature profiles, it is observed that the number of active centers
2 does not influence the reaction profiles. Considering that the pressure drop is basically the
3 consumption of monomer during the reaction, it can be inferred that the conversions of the four
4 simulations are very similar, while from the temperature profiles, despite the active sites have
5 different kinetic constants, the exothermicity of the reaction remains largely unchanged.

7 **4 | CONCLUSION**

8 The present study aimed to evaluate the influence of number of active catalytic sites in molar
9 distribution of polybutadiene. 1,3-butadiene polymerizations were performed successfully in
10 Aspen Plus 10 considering 1, 2, 3 and 4 catalytic sites.

11 It was concluded that temperature and pressure profiles are practically not changed with a
12 variation in the number of sites. Such profiles show an increase until reaching a peak and then
13 stabilize, showing similarity with those already reported in the literature.

14 Comparing values of M_n , M_w and PDI it can be confirmed they are directly related with the
15 grow of number of active sites. Values of M_n range from 3.6×10^4 to 1.4×10^5 , M_w range from
16 7.3×10^4 to 7.4×10^5 and PDI range from 2.02 to 5.24. Besides that, graphs generated shows that
17 the dispersity increase with the variation and MWD is dislocated to the right side.

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