

Nº 174889.1

**The study of 5-HMF synthesis from fructose using SGC650H
Purolite® in DMSO**

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*Trabalho apresentado no INTERNATIONAL SYMPOSIUM ON
ACID-BASE CATALYSIS, 8th., 2017, Rio de Janeiro. **Pôster...***

A série "Comunicação Técnica" compreende trabalhos elaborados por técnicos do IPT, apresentados em eventos, publicados em revistas especializadas ou quando seu conteúdo apresentar relevância pública.

1. INTRODUCTION

5-hydroxymethyl-2-furfural (HMF) is a furanic compound considered as an important chemical platform, once it can be obtained from renewable raw materials and has wide application in industry as an intermediary in the production of fine chemicals, polymers, biofuels and pharmaceuticals [1]. Several catalyst systems have been studied for HMF synthesis including homogeneous [2] and heterogeneous [3] and different solvent systems as aqueous [4], organic or biphasic [3].

This work presents the comparison of two reactor systems for the fructose dehydration to form HMF using an strong acid cationic resin as catalyst and dimethylsulfoxide (DMSO) as solvent aiming to evaluate the kinetics of the reaction.

2. EXPERIMENTAL

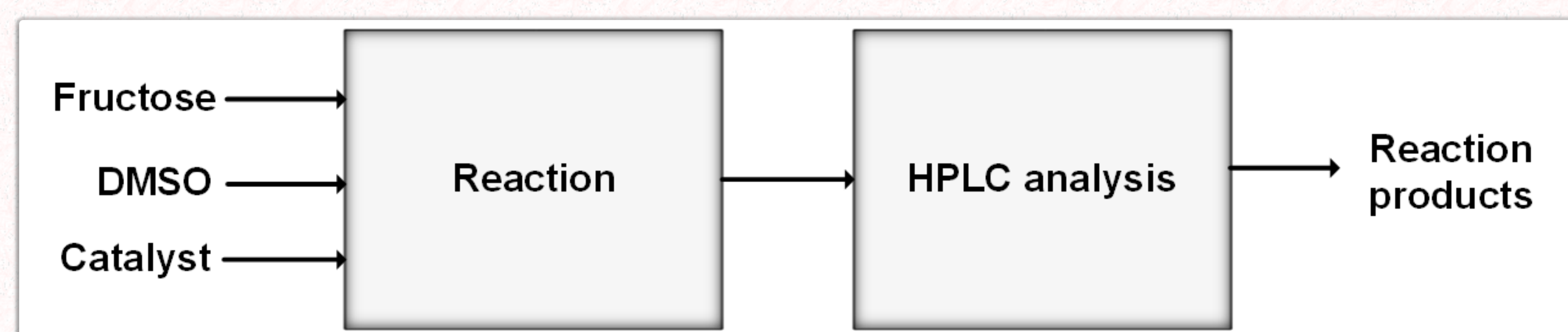


Fig. 1. Diagram of the experimental procedure.

The catalyst was an acidic resin Purolite® SGC650H with diameter in a range of (650±50) µm.

The reactions were carried out in a Parr 1.0 L batch autoclave reactor (BTR) and in a 6.5 mL continuous packed bed reactor (PBR), both constructed in 316L stainless steel.

Table 1. Experimental conditions.

Reactor	Catalyst (g/L)	[Fructose] ₀ (m/m)	Temp. (°C)
BTR	54.6	4.5 %, 13.5 %	90, 100, 110
PBR	450.0	4.5 %, 13.5 %	90, 100, 110

3. RESULTS AND DISCUSSION

The HMF yields increases with the temperature and is depressed by higher fructose concentration fed as shown in Fig. 1 and 2 for the BTR. Similar results were obtained in PBR and are presented in Fig. 3 and 4.

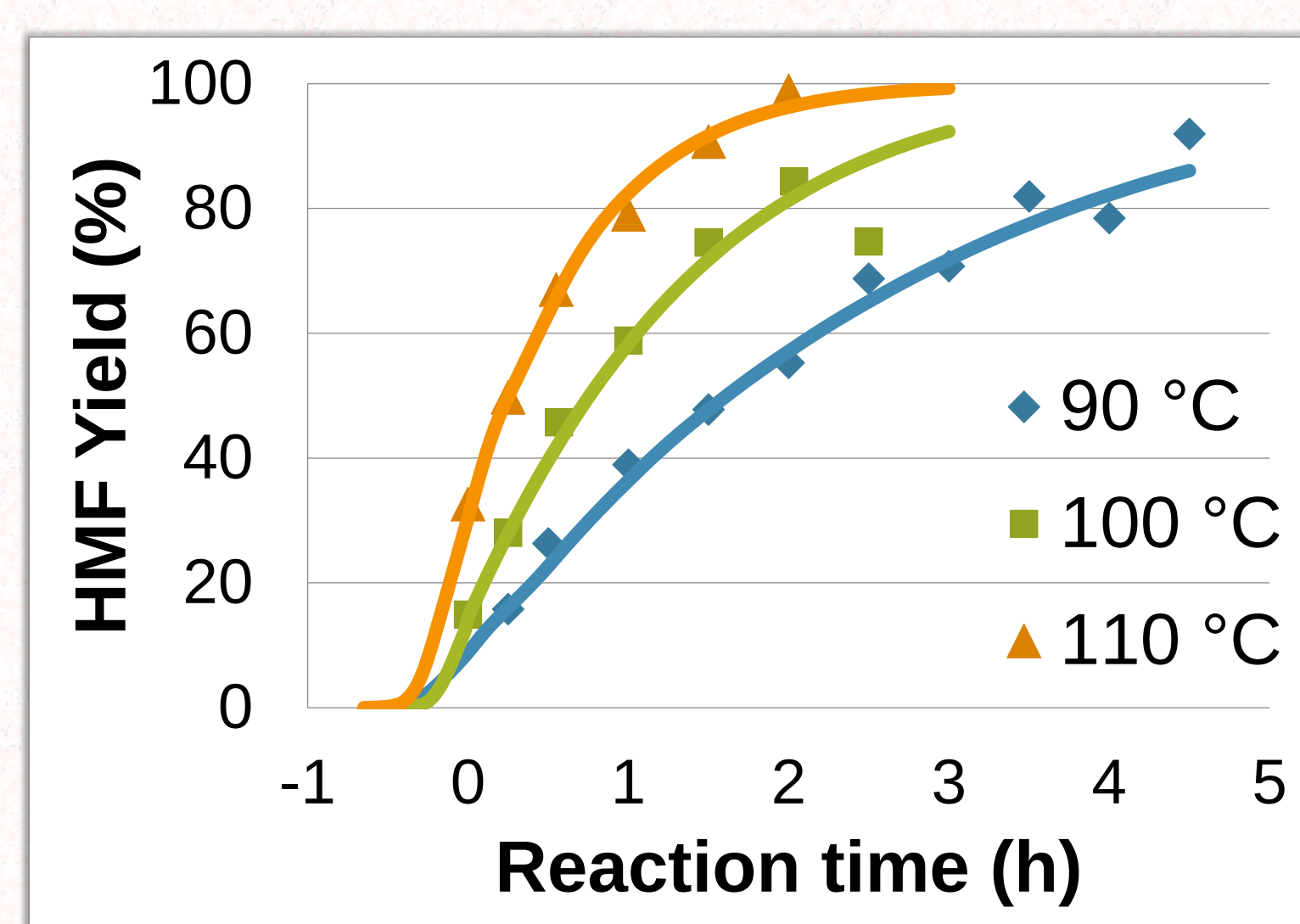


Fig. 2. Temperature effect on 4.5 % fructose using BTR, SGC650H, DMSO.

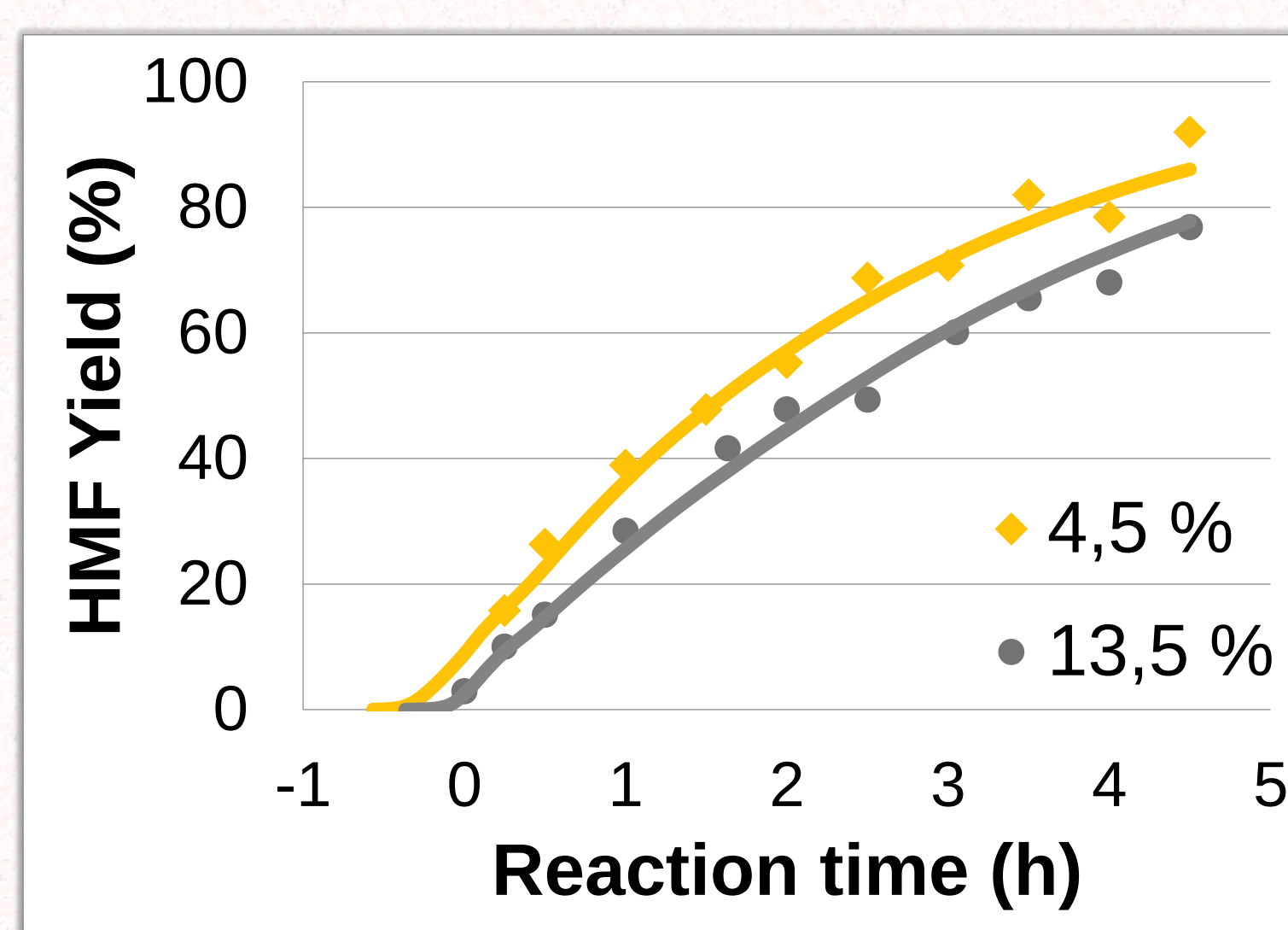


Fig. 3. [Fructose]₀ effect on reaction at 90 °C using BTR, SGC650H, DMSO.

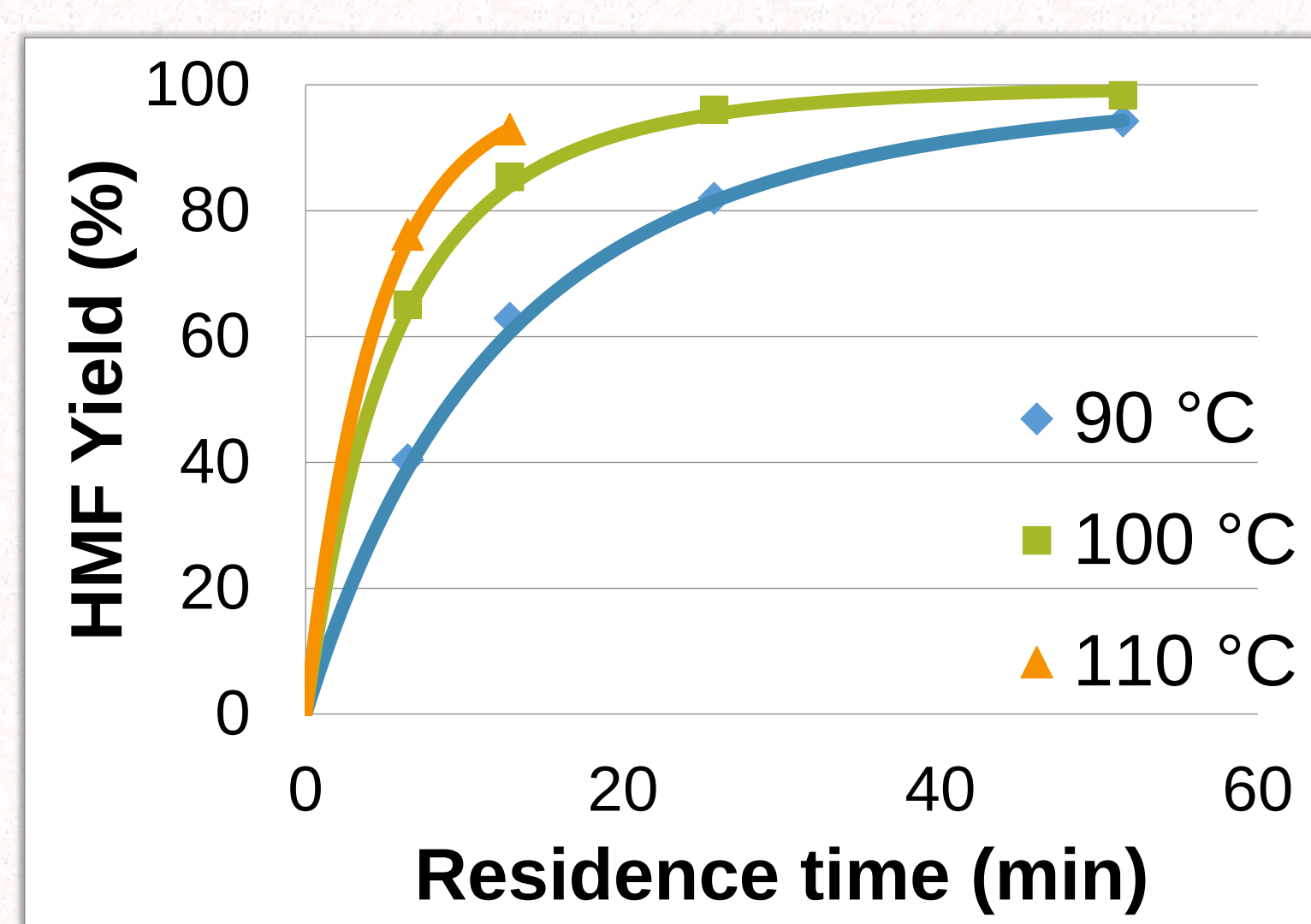


Fig. 4. Temperature effect on 4.5 % fructose using PBR, SGC650H, DMSO.

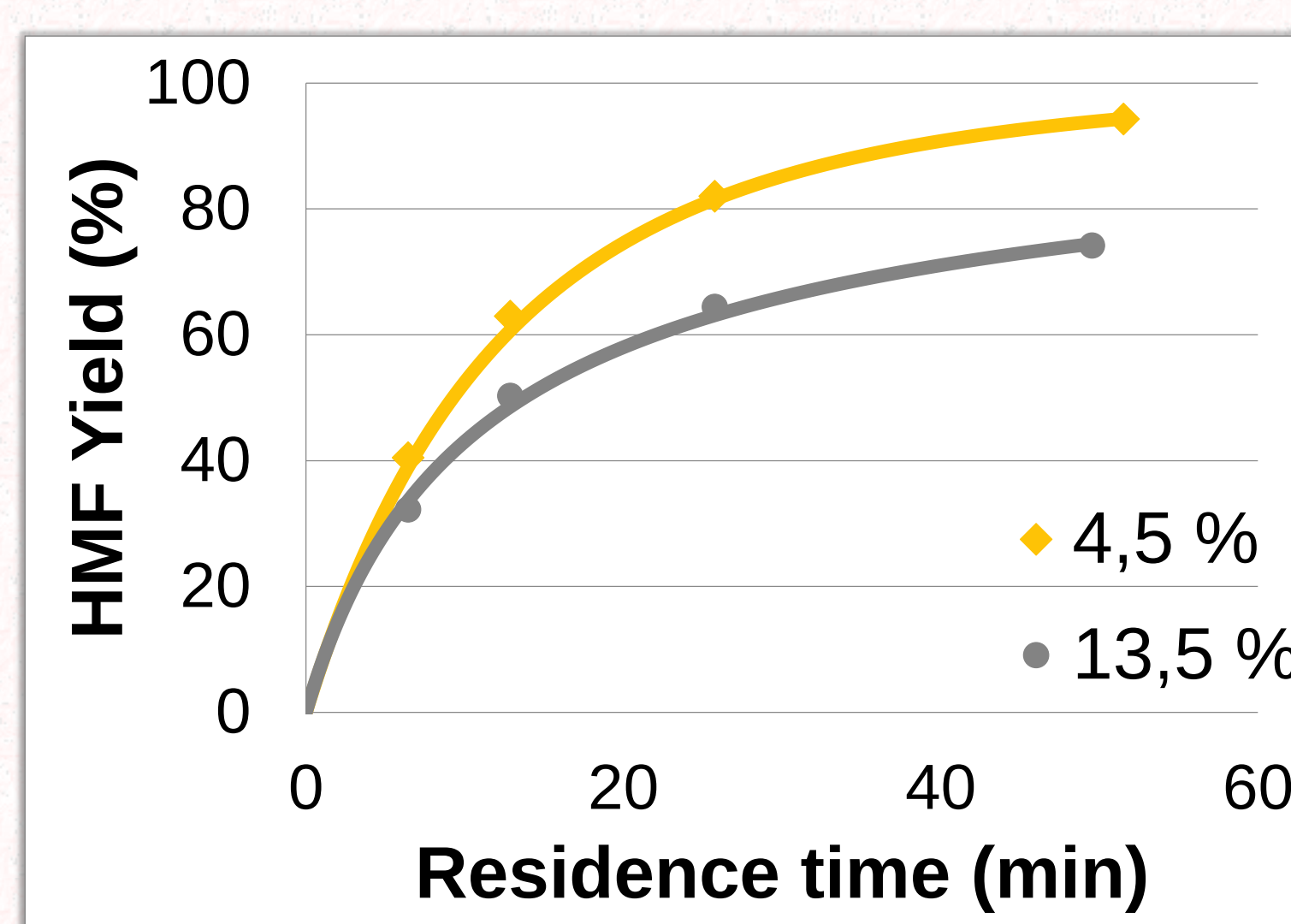


Fig. 5. [Fructose]₀ effect on reaction at 90 °C using PBR, SGC650H, DMSO.

Equations (1) to (5) were derived for the pseudo homogeneous first order reaction and show the effect of catalyst concentration which is related to the type of reactor. From these we concluded that PBR are more effective for this study because the residence time is lower than the time of reaction spent in BTR which reduces the effect of homogenous process.

$$r_F^{BTR} = -k' \cdot C_{cat}^{BTR} \cdot C_F^{BTR^n} \quad \text{Eq. 1}$$

$$-\ln(1 - X^{BTR}) = k' \cdot C_{cat}^{BTR} \cdot t^{BTR} \quad \text{Eq. 2}$$

$$r_F^{PBR} = -k' \cdot C_{cat}^{PBR} \cdot C_F^{PBR^n} \quad \text{Eq. 3}$$

$$-\ln(1 - X^{PBR}) = k' \cdot C_{cat}^{PBR} \cdot \tau^{PBR} \quad \text{Eq. 4}$$

$$\frac{C_{cat}^{PBR}}{C_{cat}^{BTR}} = \frac{r_F^{PBR}}{r_F^{BTR}} = \frac{t^{BTR}}{\tau^{PBR}} = 8,0 \quad \text{Eq. 5}$$

The intrinsic kinetic constants for pseudo first order reaction are presented in Table 2 where is possible to see the mentioned effects.

None LHHW kinetic model based on reaction limiting step (RLS) fit the data. The Arrhenius parameters present the kinetic compensation effect [5] as shown in Fig. 6 which means the model is incorrect.

Table 2. Intrinsic kinetic parameters for experiments.

Reactor	[Fructose] ₀ (m/m)	$k' \cdot 10^4 \text{ (L} \cdot \text{g}_{cat}^{-1} \cdot \text{min}^{-1})$			E_A (kJ/mol)	$\ln(k'_0)$
		90 °C	100 °C	110 °C		
BTR	4.5 %	1,024	1,961	3,335	68,35	13,46
	13.5 %	0,917	1,632	2,543	59,07	10,28
PBR	4.5 %	1,800	3,767	5,391	59,96	11,33
	13.5 %	1,575				

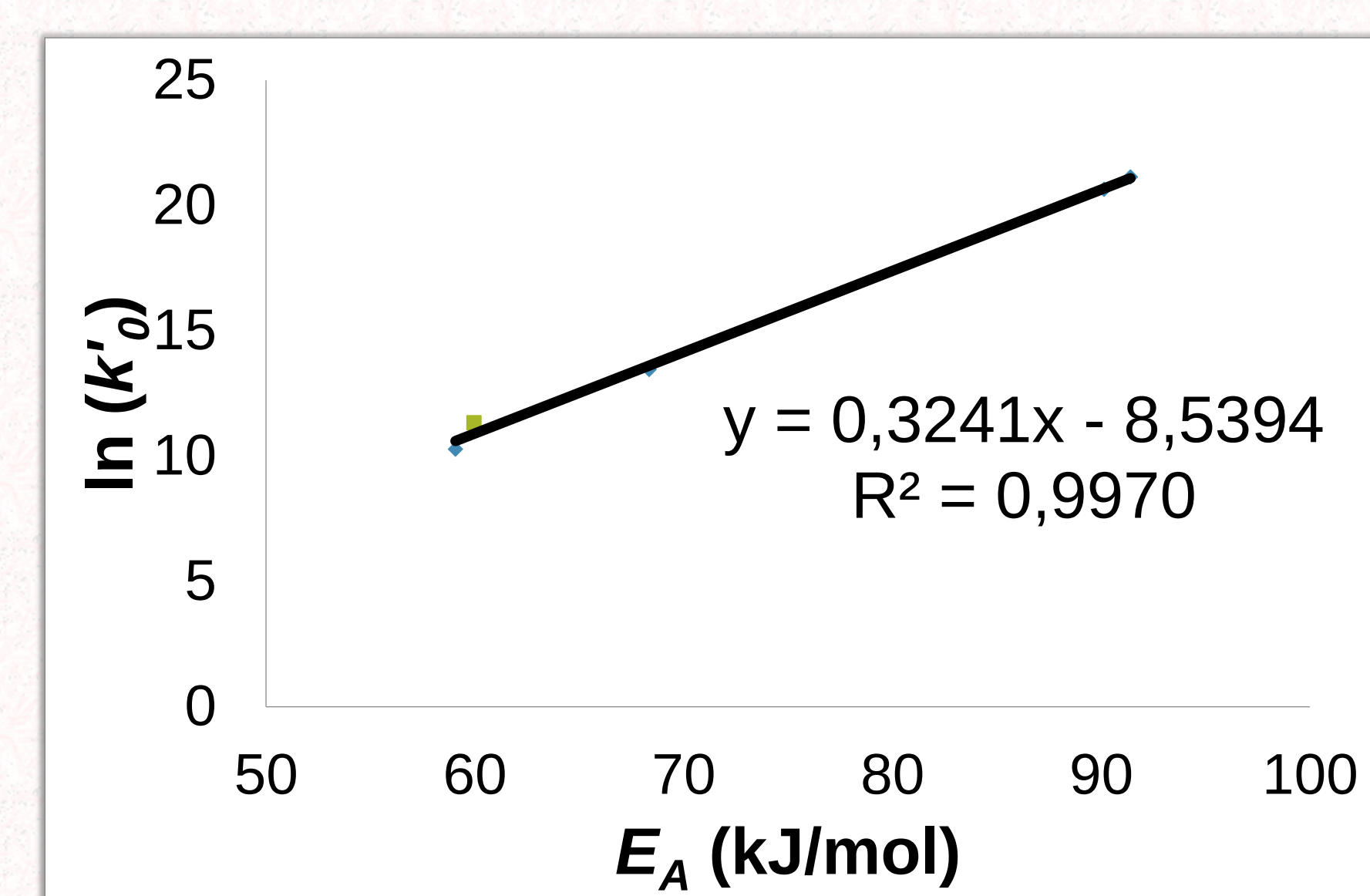


Fig. 6. Cremer Constable Diagram.

4. CONCLUSIONS

The initial rate of reactions constants depends on the temperature and the concentration fed. The global rate obtained with the PBR is higher than that for the BTR. The Arrhenius kinetic parameters for pseudo first order (E_A and k'_0), show kinetic compensation effect and then they do not represent the reaction.

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ACKNOWLEDGEMENTS