BRAZILIAN JOURNAL OF PETROLEUM AND GAS
Journal Homepage: www.portalabpg.org.br/bjpg
A publication of the ABPG
BRAZILIAN ASSOCIATION OF R&D IN PETROLEUM AND GAS

EXPERIMENTAL DESIGN FOR CO_2 CONVERSION INTO DIMETHYLCARBONATE (DMC) USING Bu_2SnO AT SUBCRITICAL CONDITIONS

[a] Ferreira, H. B. P.; [a] Vale, D. L.; [a,b] Mota, C. J. A.; [a,b] Miranda, J. L.[1]

[a] Universidade Federal do Rio de Janeiro, Instituto de Química, Rio de Janeiro, Brazil
[b] INCT Energia e Ambiente, UFRJ, Rio de Janeiro, Brazil

ABSTRACT

CO_2 conversion into dimethylcarbonate (DMC) was studied by the reaction with methanol at subcritical conditions, using dibutyltin(IV) oxide (Bu_2SnO) or dibutyltin(IV) dimethoxide ($Bu_2Sn(OMe)_2$) as catalysts. Fractional factorial and complete factorial designs were used to evaluate the most important factors capable of affecting this conversion reaction. This study found that the optimal conditions for CO_2 conversion into DMC using But_2SnO were a reaction pressure of 45 bar, a volume of methanol of 5mL, a temperature of 110°C, and a reaction time of 6 hours. The present study also employed these optimal conditions with $Bu_2Sn(OMe)_2$. Even under subcritical conditions, results showed a DMC yield (based on Sn) of 40 % using $Bu_2Sn(OMe)_2$, with TON= 1.

KEYWORDS

CO_2 fixation; DMC; factorial design; tin oxide; experimental design

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[1] To whom all correspondence should be addressed.
Address: Instituto de Química, Universidade Federal do Rio de Janeiro, 149 Athos da Silveira Ramos Av., Rio de Janeiro- Brazil - CEP 21941-909
Telephone / Fax: +55 21 2562-7820 / +55 21 2562-7559 | E-mail: jussara@iq.ufrj.br

doi:10.5419/bjpg2012-0008

1. INTRODUCTION

Carbon dioxide (CO_2) is regarded as the principal greenhouse gas **(Viola, 2002**; **Aresta, 2003**; **Jessop et al., 1995)** and has been related to the augment of the global warming **(Viola, 2002**; **Aresta, 2003)**. CO_2 from fossil fuels represents the major percentage of Green House Gases (GHG) emissions, according to IPCC reports **(IPCC, 2007)**. For this reason, different scenarios foresee a maximum of 550 ppm of CO_2-equilavent for a 2-3°C exceeding temperature. Thus, several efforts should be made to reduce GHG emissions and the goals of these reductions were proposed in Kyoto's Protocol which established for the countries of Annex I a reduction of 5 % in GHG emissions below the levels of 1990 in the commitment period of 2008-2012 **(United Nations, 1998)**.

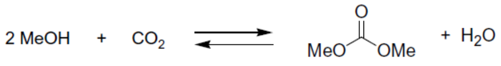
Several researches support a more sustainable economy with the development of projects that seek for GHG reduction **(Chicco et al., 2012)**. The concept of Carbon Capture and Storage (CCS) has been proposed as a tool for reducing CO_2 emissions from fossil fuels worldwide in several projects with the participation of the most important energy companies with a great diversity of projects **(CO_2 Capture Project, 2000**; **Leite et al., 2012)**. Examples of different sectors that aim GHG reductions include EOR (Enhanced Oil recovery), building design **(Georgiadou et al., 2012)**, road transport and transportation sector **(Rubin et al., 2012**; **Andress et al., 2011)**, farm biogas production **(Massé et al., 2012)** and conversion catalytic researches **(Jessop et al., 1995**; **Omae, 2006)**.

Developing countries such as Brazil are sponsoring Clean Development Mechanism (CDM) projects, such as the first CDM project approved by UNFCCC (United Nations Framework Convention on Climate Change), which was the Brazilian's "NOVAGERAR" project that captures biogas to produce energy **(Segreti and Bito, 2006)**.

CO_2 can also be used as a raw material for several synthetic processes in order to obtain products of great economic value, such as cabarmates, urethanes, lactones, pyrones, formic acid or methanol **(Jessop et al., 1995)**. The main challenge to overcome CO_2 conversion is its stability, which requires more severe conditions for it and also motivates the research on different types of catalysts to obtain reasonable results. Although some CO_2 reactions previously studied were able to produce interesting products such as methanol, formaldehyde and formic acid **(Jessop et al., 1995**; **Chiavassa et al., 2008**; **Mahajan et al., 2003)**, they also presented low efficiency and selectiveness. In addition, another challenge in CO_2 conversion is the development of processes able to be scale up for industrial use **(Omae, 2006)**.

The conversion of CO_2 specifically into dimethylcarbonate (DMC) has been of great interest and extensively studied, since this compound is a key reagent to produce several other chemicals, including polycarbonates (PC). One of the routes for DMC production from CO_2 is already in use at Asahi Chemical Industry, employing a reaction with ethylene oxide and replacing phosgene, which is extremely poisonous **(Jessop et al., 1995)**.

The study of DMC synthesis using CO_2 through the reaction with methanol began in the 1990's **(Sakakura et al., 1998)** (Equation 1). The reaction can be catalyzed by different metals, although the most used is tin, employed as an oxide compound or as an organometallic complex **(Hoffman, 1982**; **Dibenedetto et al., 2006**; **Choi et al., 1999**; **Choi et al., 2002)**.



$$2\,MeOH + CO_2 \rightleftharpoons MeO\overset{O}{\overset{\|}{C}}OMe + H_2O \qquad (1)$$

The proposed mechanism for DMC formation in Eq 1, using tin catalyst is based on CO_2 insertion in Sn-O bond of catalyst, forming a carbonate complex intermediary **(Sakakura et al., 2000)**.

Ballivet-Tkatchenko et al. (2003, **2011)** studied CO_2 conversion with methanol at 50ºC and 200 bar using SnO_2 as catalyst. These researchers found a yield of 0.3% and 4% with unsupported and supported SiO_2, respectively. **Kizlink et al. (1993**, **1994)** used dibutyltin(IV) oxide, Bu_2SnO, as the catalyst for the same reaction.

Other class of compounds used for CO_2 conversion with methanol is the alkoxides. **Aresta et al. (2008)** and **Bian et al. (2009)** proposed a catalytic mechanism with alkoxides, involving CO_2 insertion into the tin methoxide bond. **Kizlink and Pastucha (1994)** proposed CO_2 conversion with methanol into DMC using $Sn(OEt)_4$ and different dehydrating agents. They observed interesting yields in relation to the catalyst, with TON values of 1 to 1.8, using hydrating and initiator agents. **Dibenedetto et al (2006)** used polystyrene-C_6H_4-CH_2CH_2-$SnBu(OCH_3)_2$ as catalyst and obtained a yield of 0.12% at 40 bar. In other study, **Sakukara et al. (1998)** used different tin alkoxide as catalysts, such as $Bu_2Sn(OMe)_2$, $Bu_3Sn(OMe)$, $Me_2Sn(OMe)_2$, obtaining yields up to 20% in relation to the catalyst (TON= 0.2).

Although there are several works regarding CO_2 conversion, none of them has taken into account the interaction among the variables that can be relevant for its optimization. This work focuses in the optimization of CO_2 conversion into methanol at subcritical conditions using dibutyltin(IV) oxide (Bu_2SnO) or dibutyltin(IV) dimethoxide ($Bu_2Sn(OMe)_2$). Fractional factorial and complete factorial designs were done for CO_2 conversion with methanol and dibutyltin(IV) oxide in order to evaluate the most important factors in this process, as well as their influence in the reaction and the possible interactions among them.

2. EXPERIMENTAL

2.1General

Methanol (Acros, HPLC grade, 99.8%) was distilled and dried over 3A molecular sieve. Carbon dioxide was purchased from LINDE Gases, 99.999% purity. Dibutyltin(IV) dimethoxide (99%) and dibutyltin(IV) oxide (98%) were purchased from Sigma Aldrich. All of the products were used without further purification.

2.2Infrared and Raman analyses

Infrared analyses were done using Magna-IR 760 Nicolet spectrometer, in the range of 4000 to 200 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans. The platelets were prepared using cesium iodide. During the study of design of experiments, the resultant solids obtained after experiments were analyzed by infrared spectroscopy. Bu_2SnO was analyzed by infrared spectroscopy before and after the conversion reaction.

The Raman spectra were obtained at room temperature using Jobin-Yvon HR800UV spectrometer, coupled to a BX41 Olympus microscope. Excitation was provided by a He/Ne operating at 632.8 nm. A CCD detector at -170 ^{o}C was used and the resolution of the spectrometer was 1 cm^{-1}. The Raman spectra of the solids were done with D1 filter in order to prevent local heating.

2.3Catalytic tests

The initial chosen conditions for the catalytic tests were based on the already reported experiments for CO_2 conversion to DMC using tin catalysts **(Ballivet-Tkatchenko, 2003**; **Sakai, 1975**; **Yamazaki, 1978**; **Kizlink, 1994**; **Keller et al., 2010**; **Sakakura and Kohno, 2009**; **Ma et al., 2009**; **Sakakura et al., 1999**; **Ballivet-Tkatchenko et al., 2000**; **Choi et al., 2002**; **Sakakura et al., 2000**; **Aresta et al., 2006)**.

The catalytic tests were carried out in a 100mL Parr 4560 reactor, with 0.5g of $Bu_2Sn(OMe)_2$ or Bu_2SnO dissolved in methanol (5 -10mL) and CO_2 at an initial pressure of 300-500 psi (21 to 35 bar). The temperature range was 80 to 120^{o}C and the reaction time was from 60 to 180 minutes. The pressure measured during the reaction at 80 to 120^{o}C temperature range was 28 to 70 bar.

The final reaction mixture was centrifuged and the solid phase was dried at 60^{o}C in vacuum line (10^{-1} mbar) and further analyzed by infrared spectroscopy. The liquid phase was analyzed in triplicate by gas chromatography coupled with mass detector – (Agilent 7890A CG coupled with Agilent 5975C) using an HP-5 column (30m x 0.32mm x 0.25µm film). The conditions used in chromatography analysis were a gradient temperature of 40-200^{o}C, with an initial isotherm at 40^{o}C, using nitrogen as the carrier gas and a detector temperature of 280^{o}C.

DMC quantification analysis was done in the liquid phase using chromatography calibration curves with an auto sample injector in the concentration range of 1.29×10^{-3} $mol.L^{-1}$ to 5.00×10^{-2} $mol.L^{-1}$ in methanol as a solvent, obtaining $R^2 = 0.9949$. All standard samples and pos-reaction liquid phase were analyzed in triplicates.

2.4Experimental designs

For the optimization of the CO_2 conversion to

Table 1. Plan of experiments for FFD 2^{4-1} design for four variables with twofold repetition of the central point.

Exp	Temperature (°C)	Time (min)	CO_2 Pressure (Psi)	Volume of MeOH (mL)	Area (DMC)	Standard Deviation (%)
1	80	60	300	5	112436	0.2
2	120	60	300	10	481670	4.9
3	80	180	300	10	253924	4.8
4	120	180	300	5	1566593	3.4
5	80	60	500	10	160807	3.4
6	120	60	500	5	948646	4.7
7	80	180	500	5	110998	4.9
8	120	180	500	10	1793243	3.6
9	100	120	400	7.5	942443	
10	100	120	400	7.5	987874	

DMC, a fixed amount of Bu_2SnO (500 mg) was used in all experiments. The choice of Bu_2SnO as the catalyst, instead of the more often used $Bu_2Sn(OMe)_2$, was based on the cost, an aspect that should be considered for further applications of this study.

Fractional factorial design (FFD) **(Neto et al., 2002)** was employed as a first screening design for CO_2 conversion into DMC using dibutyltin (IV) oxide, Bu_2SnO. In this study, FFD 2^{4-1} was done with ten experiments, carried out randomly, in order to evaluate and reduce the number of variables that influence this reaction, as well as the interactions among them. Each experiment was done in duplicate and analyzed twice. The variables used for this design were the following: reaction temperature, CO_2 pressure, reaction time and volume of methanol. These variables have been selected based on a screening of several already reported experiments **(Keller et al., 2010**; **Sakakura and Kohno, 2009; Ma et al., 2009**; **Sakakura et al., 1999**; **Ballivet-Tkatchenko et al., 2000**; **Choi et al., 2002**; **Sakakura et al., 2000**; **Aresta et al., 2006)** using the same reagents. The experimental response analyzed for this design was the peak area related to DMC obtained from the chromatograms (retention time = 2.28 min), since it is proportional to the analyte concentration **(Harris, 2001)**. The percentage of conversion in relation to DMC could not be calculated from its concentration because in some analyses it was below the quantification limit.

The data obtained from FFD have been used for the second step of this design, a *Complete Factorial Design* (CFD) **(Neto et al., 2002)**, in which only the variables with greater significance were employed. The analyses done for CFD, however, have been done in a different day of those used for FDD.

3. RESULTS AND DISCUSSION

3.1Experimental Design

3.1.1 The fractional factorial design (FFD)

All variables, levels and their responses used for FFD 2^{4-1} are shown in Table 1. Ten experiments were carried out in a random way and the responses of the experiments were their peak areas of DMC, which are shown in fifth column of Table 1. In addition, the standard deviations percentages were all below 5% which indicated the reproducibility of all tests.

Pareto´s chart (Fig. 1), which bar length is proportional to the absolute value of the standardized effects, was constructed using the data from Table 1. This chart was used to evaluate the significance of each variable in a 95% level of confidence. It can be observed in Fig.1 that the most significant variable was the reaction temperature, followed by reaction time, both with positive effects. Other variables such as volume of methanol, CO_2 pressure and curvature, however,

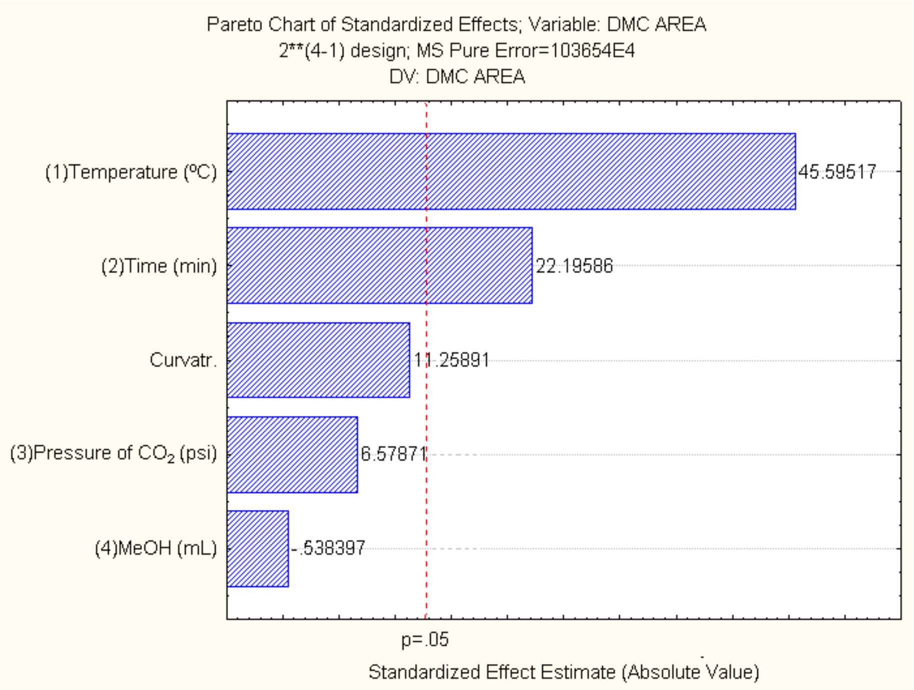


Figure 1. Pareto´s Chart from 2^{4-1} design for Bu_2SnO.

presented a level of confidence lower than 95 % and were deemed not significant.

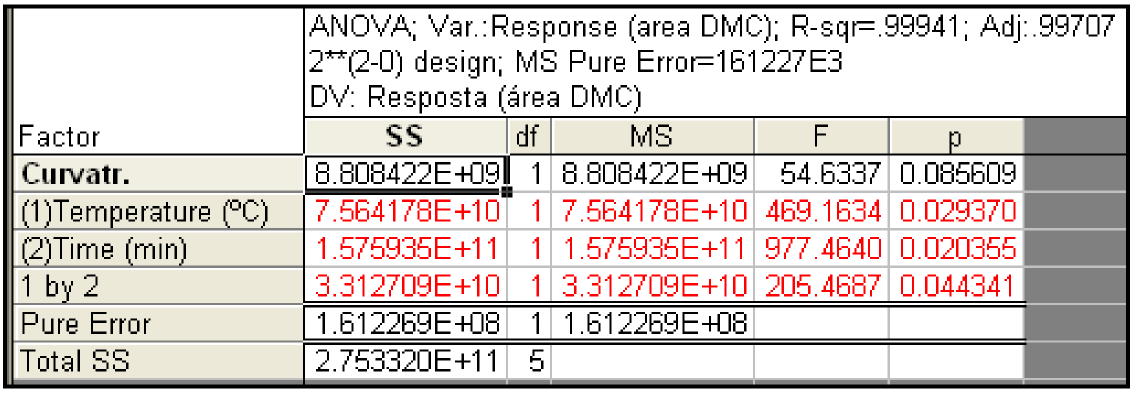
From the variance analysis, one can observe that the lack of fit (0.057) and the curvature (0.052) of the model were not significant at a level of 95% of confidence in the tested conditions. Furthermore, one can conclude that the used model was able to explain 85% of the variance and presented a small pure mistake (smaller than 5), showing data consistency.

3.1.2 Complete factorial design

After evaluating the principal factors that influenced CO_2 conversion into DMC with Bu_2SnO using FFD 2^{4-1}, and checking the validation of the method, a complete design was done. Thus, a 2^2 complete factorial design was done regarding the central point with the following two variables: reaction temperature and reaction time. The values of the two variables used, as well as the DMC areas, are shown in Table 2. The non significant variables were fixed as follow: volume of methanol at 5mL and CO_2 pressure at 400 psi (28 bar). For the evaluation of the proposed model for the optimization of reaction temperature and reaction time, a variance of 99.9 (R-sqr = .99941 in Fig. 2) was observed, with a small pure error (1.612269E+08, Fig. 2), indicating a good accuracy with the experimental results **(Neto et al., 2002)**. In addition, according to Figure 2, the curvature was not significant at a level of confidence of 95% under the tested conditions since its p-value (0.085) was higher than the set value for the model (0.05).

Table 2. Values used for each variable in a 2^2 factorial design.

Temperature (°C)	Time (min)	Area (DMC)	Standard Deviation
120	180	724450	2.0
170	180	631428	1.9
120	360	1303439	1.5
170	360	846400	1.2
145	270	966687	2.2
145	270	948730	1.6



ANOVA; Var.:Response (area DMC); R-sqr=.99941; Adj:.99707
2**(2-0) design; MS Pure Error=161227E3
DV: Resposta (área DMC)

Factor	SS	df	MS	F	p
Curvatr.	8.808422E+09	1	8.808422E+09	54.6337	0.085609
(1)Temperature (°C)	7.564178E+10	1	7.564178E+10	469.1634	0.029370
(2)Time (min)	1.575935E+11	1	1.575935E+11	977.4640	0.020355
1 by 2	3.312709E+10	1	3.312709E+10	205.4687	0.044341
Pure Error	1.612269E+08	1	1.612269E+08		
Total SS	2.753320E+11	5			

Figure 2. Table of ANOVA for the factorial design 2^2 for the conversion of CO_2 to DMC using bu_2SnO as catalyst.

The adjustment of the model can be observed by the comparison between experimental and predicted values obtained from 2^2 design using Bu_2SnO (Fig. 3), which shows a good dispersion of the points, indicating a well adjusted model.

A surface plot of a 2^2 factorial design was done (Fig. 4) in order to evaluate the optimal reaction conditions for CO_2 conversion into DMC. From the surface plot (Fig. 4), it can be observed that the optimal conditions for this reaction were around 110°C and 6 hours of reaction time. Besides temperature and reaction time, Table 3 also presents other important variables for the optimal conditions, such as methanol volume and pressure reaction.

3.2Infrared and Raman analyses of Bu_2SnO

The infrared spectra of the resultant solids from all analyzed experiments in FFD 2^{4-1} are shown in Fig. 5. The principal bands characteristics of the Bu_2SnO could be observed, such as ν C-O in 1030 to 1070 cm^{-1}, as well as those relative to the Sn-ligand bonds, the symmetric and asymmetric ν Sn-C bands in 500-600 cm^{-1} region and ν Sn-O around 500 cm^{-1}, respectively **(Bradley, 2001)**.The infrared data from experiments 1 to 8 in Fig. 5 presented small changes when compared to the catalyst before the reaction, showing that Bu_2SnO should remain stable after the conversion reaction.

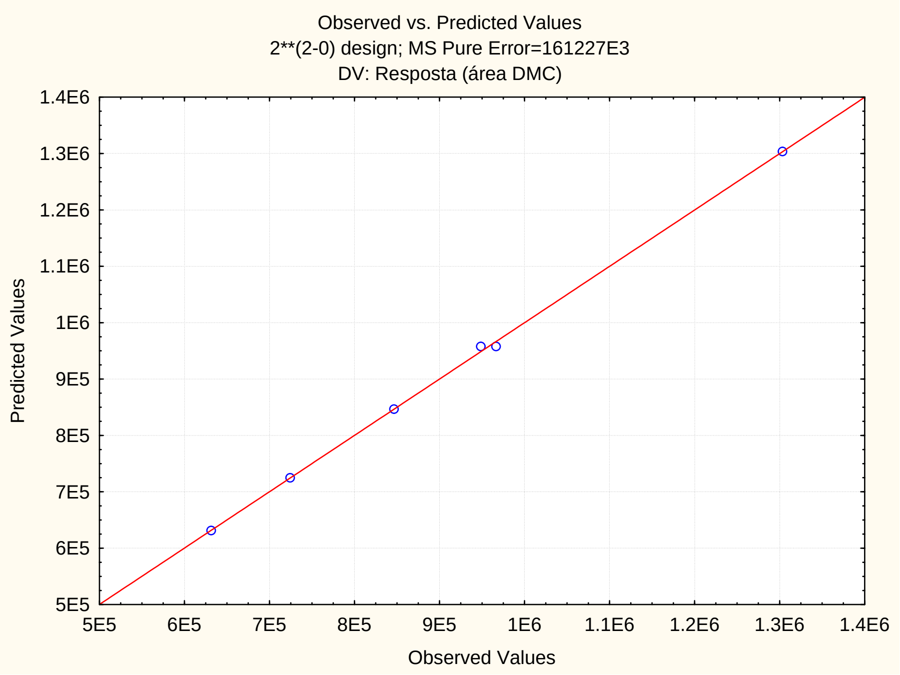


Figure 3. Comparison between experimental and predicted values obtained from 2^2 design using Bu_2SnO.

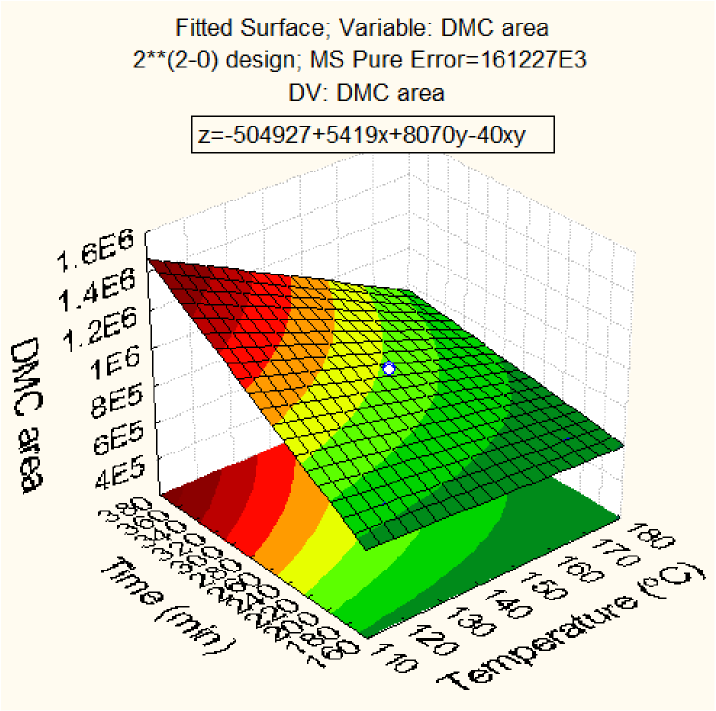


Figure 4. Surface plots for a 2^2 factorial design.

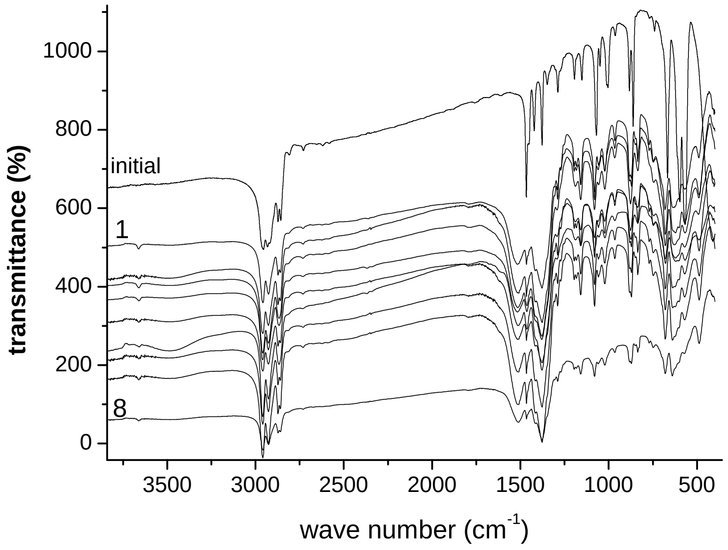


Figure 5. Infrared spectra (4000 to 500 cm^{-1}) of the solids from all experiments done for 2^{4-1} FFD using Bu_2SnO. (From top to bottom, the catalyst before the conversion reaction- initial, and the solids after the experiments 1-8, respectively).

Raman spectra of the Bu_2SnO (Figure 6) before and after reaction confirmed the infrared data and also indicated small changes, probably due to the conversion of Bu_2SnO into dialkyltin oxide, which is the key intermediate for this reaction, as reported by **Sakakura et al. (2000)**. Thus, the new observed bands after the catalytic test were typical of alkoxides, at 1070 cm^{-1} and 580-600 cm^{-1}, relative to ν C-O and ν Sn-O, respectively **(Bradley et al., 2001)**.

The analyses of the Raman spectra of the other catalyst used, $Bu_2Sn(OMe)_2$, is shown in Fig. 7. The

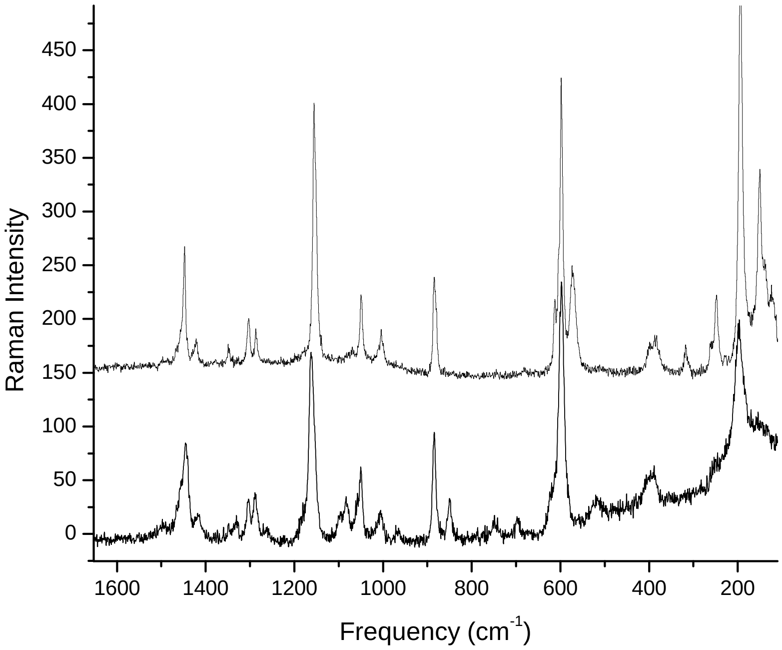


Figure 6. Raman Spectra of Bu_2SnO before (b) and after (a) catalytic test.

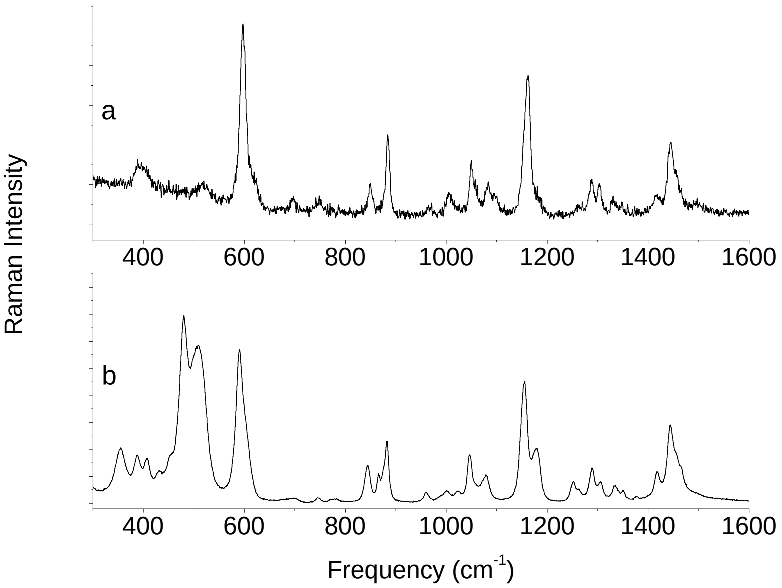


Figure 7. Raman Spectra of $Bu_2Sn(OMe)_2$ before (b) and after (a) catalytic test.

profiles of the Raman spectra of $Bu_2Sn(OMe)_2$ before (Fig. 7b) and after catalytic reaction (Fig. 7a) were similar, with an exception of the bands around 500 cm^{-1} and considering the lower intensity of the bands after the reaction. The bands in the region around 500cm^{-1} could be assigned to ν Sn-C and ν Sn-O stretching modes **(Bradley et al., 2001)**. In Fig 7, one of these bands has its intensity diminished and the other one has the bands disappeared after the reaction, which was probably due to a condensation reaction.

3.3 CO_2 Conversion and Comparison of the Catalysts Performance

Using these optimal conditions described in

Table 3. Optimal conditions for CO_2 conversion with methanol into DMC, using Bu_2SnO as catalyst.

Optimal conditions for CO_2 conversion into DMC using Bu_2SnO	
Reaction Pressure	45 bar
Volume of methanol	5 mL
Temperature	110 °C
Time	6 hours

Table 3, the experiment tested $Bu_2Sn(OMe)_2$ as catalyst for CO_2 conversion with methanol, using the same reactor and CG used for Bu_2SnO. CO_2 conversion using Bu_2SnO as catalyst had a TON of 0.2 (in relation to DMC) whereas using $Bu_2Sn(OMe)_2$ had a TON=1 (Table 4). These are reasonable good results in comparison with the already reported data and considering the conditions used in this study.

In order to make a better comparison among the catalysts and experimental conditions, the study selected from Table 4 experiments on CO_2 conversion, using the catalyst $Bu_2Sn(OMe)_2$ and proximal reaction conditions. The experiments collected in Table 4 presented pressure varying from 25 to 200 bar and temperature ranging from 110 to 180°C, whereas the reaction time varied from 6 to 27h. Nevertheless, it is important to evaluate the amount of energy necessary in each of this CO_2 conversion tests in order to know how energetically and economically is its viability. Higher temperature reaction, time and pressure also imply in higher energy demand and costs for the application in a large scale.

Experiments 1 and 2 are related to our work. It is interesting to observe that even employing subcritical conditions, 45 bar and 110°C, and few hours of reaction (6 h), TON values using Bu_2SnO and $Bu_2Sn(OMe)_2$ were 0.2 and 1, respectively (TON= mol of DMC/ mol of catalyst). Experiment 4 presented a higher TON (3) than the one found in this study, however it employed higher pressure reaction, temperature and reaction time, implying more energetic conversion. The difference in pressure used in Experiment 4, 200 bar, is more than four times larger than the pressure used in the present work. Experiment 7 presented almost the same TON as this work, however with much higher time reaction and the employment of a dehydrating agent, DCC- N,N'-

Table 4. Comparison of CO_2 Conversion into DMC using $Bu_2Sn(OMe)_2$ and Bu_2SnO in different Conditions.

Experiment	**Catalyst**	**Dehydrating agent**	**Conditions**	**DMC yield (TON)**	**Ref.**
1	$Bu_2Sn(OMe)_2$	-	110°C, 45 bar, 6 h	1	This work
2	Bu_2SnO	-	110°C, 45 bar, 6 h	0.2	This work
3	$Bu_2Sn(OMe)_2$	-	150°C, 66 bar, 6 h	0.32	Kizlink, 1993
4	$Bu_2Sn(OMe)_2$	-	150°C, 200 bar, 12 h	3	Ballivet-Tkatchenko, 2003
5	$Bu_2Sn(OMe)_2$	-	100°C, 30 bar, 27 h	0.1	Sakai, 1975
6	$Bu_2Sn(OMe)_2$	-	100°C, 50 bar	0.98	Yamazaki, 1978
7	$Bu_2Sn(OMe)_2$	DCC*	150°C, 25 bar, 20 h	1.2	Kizlink, 1994
8	$Bu_2Sn(OMe)_2$		180°C, 28 bar, 20 h	1	Kizlink, 1994

*N,N'-Dicyclohexylcarbodiimide (**DCC**); TON = Turnover Number, mol DMC/ mol of catalyst.

Dicyclohexylcarbodiimide. The problem with this use is its cost and recyclability **(Sakakura and Kohno, 2009)**. Experiment 8 had a greater time reaction, 20h, and a greater temperature, presenting the same TON value than this work. Experiment 6 had a very close TON to this work, 0.98, using a slightly greater pressure. The other experiments had values of TON smaller than 1.0.

All experiments done in this work were selective to DMC formation. Thus, one can conclude that it is possible to employ less energetic, *subcritical conditions*, and achieve reasonable results for CO_2 conversion by employing experimental design and thus, reducing the number of analyses and the cost of the study.

4. CONCLUSIONS

CO_2 conversion into DMC was optimized using factorial designs. Initially, the experiments carried out a preliminary analysis of all possible variables using fractional factorial designs. After identifying the most significant variables, which were temperature and time, a 2^2 factorial design was applied. The relevance of applying these models is the possibility of evaluating the interactions between the variables, which are neglected in univariate optimizations.

The use of optimization and experimental designs for CO_2 conversion evaluation, which remains unreported, may be an interesting tool to develop more sustainable experiments in this area. In this study, values of TON equal to 0.2 for Bu_2SnO and 1 for $Bu_2Sn(OMe)_2$ were achieved, which are in good agreement with the data already reported, but with less reaction time. The use of this approach implies in the consumption of a smaller amount of energy and reagents and, consequently, in less carbon input during research and development stages, which certainly contributes to a more environmental friendly chemistry.

ACKNOWLEDGEMENTS

- Raman analyses were done in “Núcleo de Catálise” Laboratory, NUCAT/PEQ/COPPE-UFRJ
- Thanks to the financial support from CAPES, CNPq and FAPERJ.
- Thanks to “Programa de Recursos Humanos- PRH 01- Químico de Petróleo”- “convênio ANP/IQ-UFRJ”.

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