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# An extreme vertices mixture design approach to the optimization of methylal production process using p-toluenesulfonic acid as catalyst

Sajjad Damiri\*, Hamid R. Pouretedal, Oveis Bakhshi

Department of chemistry, Malek-e-ashtar University of Technology, Shahin-shahr, Isfahan, Iran

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## ABSTRACT

In the present study, the synthesis process of methylal, as a diesel fuel improver, by acetalization of methanol and formaldehyde is introduced using p-toluenesulfonic acid (PTSA) as an efficient catalyst. The catalytic behavior of PTSA is compared to sulfuric acid and cationic exchange resin of Amberlite IR-120, and also in the presence of PTSA, the two responses of methylal production capacity and synthesis rate in a batch process were optimized using statistical modelling of extreme vertices mixture design of experiments results by Minitab software and based on three variables of methanol, formalin and PTSA catalyst proportions. Statistical analysis of the results showed that predicted values for the two responses be in good agreement with experimental values. The results showed that the high production rate mainly was affected by the increasing of catalyst proportion in the mixture and the amount of methanol and formalin and also their stoichiometric ratio determine the production capacity of process. The optimized experimental conditions for the synthesis of methylal by the highest production capacity and rate were achieved from the mixture formulation contained 56.23 wt.% methanol, 37.91 wt.% formalin solution (35.1 wt.%), and 5.86 wt.% of PTSA catalyst, with production capacity of 43.8 mL methylal per 100 mL of initial reactant mixture, production rate of 27.35 mL/h, and experimental relative error of 2.7% and 7.4%, respectively. This study has shown that mixture experimental design could efficiently be applied for the modeling of catalytic process of DMM, and it is an economical way of obtaining the maximum amount of information with the fewest number of experiments.

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## 1. Introduction

Methylal ( $\text{CH}_3\text{-O-CH}_2\text{-O-CH}_3$ ), also known as dimethoxymethane (DMM), is a colorless flammable liquid with a low boiling point and low viscosity that contains 42% oxygen by weight oxygen. It is soluble in diesel fuels and can be added to fuel to improve its cetane number (Vertin et al., 1999; Liu et al., 2012). The addition of dimethoxymethane (DMM) and dimethoxypropane (DMP) to fuel show an appreciable reduction of emissions such as smoke density, particulate matter and marginal increase in the performance when

compared with normal diesel run (Liu et al., 2012; Sathiyagnanam and Saravanan, 2008). On the other hands, DMM is often considered a “green” solvent, used in a variety of applications, such as inks and coatings, contact glue, industrial cleaning aerosols, cosmetics, pharmaceuticals, chemicals synthesis, textile and polyurethanes. In paint cleaning applications it can be used to replace dichloromethane as a solvent (Vertin et al., 1999; Liu et al., 2012).

DMM can be manufactured by oxidation of methanol or by the reaction of formaldehyde with methanol. Among the catalysts used in the attempt to synthesize DMM

\* Corresponding author. Tel.: +98 314 591 2253; fax: +98 314 522 0420.

E-mail address: [s.damiri@mut-es.ac.ir](mailto:s.damiri@mut-es.ac.ir) (S. Damiri).

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directly, a number of them include Re oxide and Re-based mixed oxides supported on  $V_2O_5$  and  $Fe_2O_3$  (Yuan and Iwasawa, 2002), the bulk and supported Keggin structures ( $H_4PVMo_{11}O_{40}-SiO_2$ ) (Liu and Iglesia, 2003),  $RuO_2-Al_2O_3$  (Liu and Iglesia, 2005), Ru/Sn catalysts (Anthony and McElwee-White, 2005),  $V_2O_5/TiO_2$  with enhanced surface acidity (Fu and Shen, 2007),  $H_4SiW_{12}O_{40}/SiO_2$  modified with  $MnCl_2$  (Zhang et al., 2008), the mesoporous V–Ce–Ti–O oxides (Liu et al., 2008), the sulfated or acid modified  $V_2O_5-TiO_2$  (Zhao et al., 2010; Lu et al., 2011; Guo et al., 2010), the bifunctional  $VO_x/TS-1$  zeolite catalysts with enhanced redox and acidic character via doping  $SO_4^{2-}$  and  $PO_4^{3-}$  (Chen et al., 2011), and also over a bifunctional  $V_2O_5/ZrO_2-Al_2O_3$  with synergistic effect of the redox and acidic components (Zhao et al., 2013). However, the catalytic system with the best productivity for this reaction appears to be industrial Fe–Mo as reported recently by Dumeignil et al. (Gornay et al., 2010; Thavornprasert et al., 2014; Cardona and Parmeggiani, 2015).

In conventional processes, DMM is produced in industrial scale via acetalization of methanol with formaldehyde over acidic catalysts, such as sulfuric acid. But sulfuric acid results in severe corrosion behavior and some difficulties in waste disposal (Zhang et al., 2011). Thus, solid acid catalysts including cation exchange resins (Liu et al., 2012; Zhang et al., 2011), silicotungstic heteropoly acid  $H_4SiW_{12}O_{40}$  (STA) (Danov et al., 2004), the sulfonated fluoroalkylene resin derivatives and crystalline aluminosilicates (Masamoto et al., 1990; Satoh and Taniyawa, 2002) were developed and have now been used widely for such advantages as elimination of corrosion, ease of recycle, and mild reaction conditions, but they may degrade and cause clogging of the reactor, lose their activity under exploitation, and need either regeneration or replacement (Cardona and Parmeggiani, 2015; Danov et al., 2004).

Conventionally, the methylal production is of batch process and the reaction is equilibrium-limited, thus continuous removal of methylal and water from the reaction system will lead to an increased efficiency of the synthetic process (Wu et al., 2006). Hence, catalytic distillation, in which the reaction and separation take place simultaneously in a single operation unit, has been used for methylal synthesis (Liu et al., 2012), but an azeotrope (92.2% methylal and 7.8% methanol) boiling at 41.9 °C is formed on the top of the distillation column. In order to obtain high-purity methylal, many approaches have been proposed in the last years such as extractive distillation with water (Liu et al., 2012; Zhang et al., 2011).

p-Toluenesulfonic acid (PTSA or pTsOH) or tosylic acid (TsOH) is an organic compound with the formula  $CH_3C_6H_4SO_3H$ . It is a white solid that is soluble in water, alcohols, and other polar organic solvents. PTSA use in organic synthesis as an “organic-soluble” acid catalyst, such as in the acetalization of aldehydes (Griesser et al., 2003), esterification of carboxylic acids (Ren et al., 2013), alkylation of the aromatic nucleus (Mahindaratne and Wimalasena, 1998), and transesterification of esters (Gao et al., 2014). Hayyan et al. (2014) used PTSA as pretreatment catalyst along with an alkali catalyzed transesterification, which got a fatty acid methyl ester (FAME) yield of 76.62%. Guan et al. (2009) obtained a FAME yield of 97.1% with PTSA as catalyst and dimethyl ether as co-solvent. Also, De Jong et al. (2009) studied the kinetics of esterification of myristic acid with isopropanol and n-propanol catalyzed by PTSA. The recycling and reusing of homogeneous catalysts are common and reviewed by Cole-Hamilton (2003). Other researchers introduced PTSA as a convenient, recoverable, safe, selective and low cost catalyst for alkylation

of the aromatic nucleus (Mahindaratne and Wimalasena, 1998). The reports on the recycling and reusing of PTSA is limited, but about other sulfonic acid compounds some reports was provided (Fernandes et al., 2012).

The main purpose of this study was to investigate the capabilities of the new catalyst of PTSA on the methylal production process from acetalization of methanol and formalin reactants, and to optimize and study the effects the catalyst and reactants proportions in a batch production systems on the production capacity and production rate of DMM. In the industrial production processes, the high yield of methylal per specified volume of the reactants, and the increasing of production rate are very important for improving the production capacity. Using the mixture design of experiments for seeking the optimum conditions for a multivariable system, is an efficient procedure for strategic planning and executing experiments so that the data obtained can be analyzed to yield valid and objective conclusions. The standard mixture designs for fitting standard models are simplex-lattice, simplex-centroid, and extreme vertices designs. In many situations, there will be both upper and lower bound constraints on the components. In this case, the entire simplex design cannot be used, and the feasible region will be some polytope. The extreme vertices designs are most appropriate for these situations.

## 2. Experimental

### 2.1. Materials and instruments

Formalin (35.1 wt.% formaldehyde, industrial grade) was purchased from Sina Chemical Industries Co. (Iran), and methanol (99.5 wt.%, industrial grade) was obtained from Zagros Petrochemical Company (Iran). The concentration of formaldehyde solutions were determined according to ASTM D2194 – 02(2012) Standard Test Method. p-Toluenesulfonic acid (purity; 98.5% wt.%, and water content; 9.5–11.5 wt.%) and cation exchanger Amberlite IR-120 (water content; 56.0 wt.%) were purchased from Sigma–Aldrich Company. All reagents were used as received. For the purification process of methylal, demineralized water with conductance  $<5.0 \mu S$  was used. The sample compositions were analyzed by gas chromatography (Shimadzu LC-6A) equipped with a flame ionization detector (FID) and GDX-403 steel column. Also mass spectrum of products were characterized using a gas chromatography–mass spectrometry system, Agilent-7890A model with electron impact ionizer. IR spectra were recorded on a Perkin Elmer spectroscope, and  $^1H$  NMRs were recorded on a Bruker (400 MHz) spectroscope.

### 2.2. Experimental setup

All experiments were carried out in a laboratory-scale glass reactor,  $V=500.0$  ml, equipped with a water jacket, two ground-glass joints connecting the reactor with a reflux condenser and a thermometer, and a sampler. To exclude hot spots, the reaction mixture was stirred with a magnetic stirrer. A constant temperature in the reactor was maintained by water circulating between the thermostat and the reactor jacket, with the temperature monitored within the latter.

The reaction mixture was prepared by mixing 110.0 mL methanol (M), 100.0 mL formaldehyde (FA) solution, and the catalyst in the range of 1–6 wt.% to achieve the desired ratio of the reactants. Whereupon the required amount of the

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