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# Optimization and statistical modeling of catalytic oxidation of 2-propanol over $CuMn_mCo_{2-m}O_4$ nano spinels by unreplicated split design methodology

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ABSTRACT

Optimization of 2-propanol oxidation over $CuMn_mCo_{2-m}O_4$ nanospinels was carried out by a split design method. 15-term model was proposed to fit the experimental data. The model revealed that both whole plot and subplot variables have significant effects on conversion of 2-propanol. The model predicted the interaction of subplot and whole plot variables as well as their importance. The maximum conversion of 2-propanol was observed over $CuMn_2O_4$ ($x_1 = 0.33$, $x_2 = 0$, $x_3 = 0.67$) at calcination and reaction temperatures of 800 °C ($z_1 = 1$) and 300 °C ($z_2 = 1$), respectively. The predicted response and the response obtained from experiment for optimum conditions were 93.36 and 96, respectively.


## 1. Introduction

The efficient use of experimental design methodology is an important requirement for fast and reliable progress in many branches of today's society, including drug, food, polymer, etc. [1]. Generally, in mixture studies the interest is in developing better or innovative formulations with optimum characteristics (responses) able to satisfy determined requirements. These characteristics will be one or more properties of the mixture, represented by experimentally measured responses. With regard to these characteristics, we may evaluate the nature of the different components involved in the formulation and theirs interactions between each other. These interactions could not be studied by classical approach. In addition, in varying the proportions of different mixture components, it is important to identify the controllable factors. The existence of some particular constraints, the so-called mixture constraints, explains why specific experimental designs and techniques used in data analysis have been developed and used for mixture studies [2]. In many real-life situations we are confronted with a combination of mixture and process variables, which influence the response of systems under survey. Optimization problems in chemistry often involve the adjustment of large numbers of variables in order to obtain the ideal set of experimental conditions that produce the most desirable results. Therefore, it is not surprising that statistical mixture designs are being applied ever more frequently to solve a variety of problems that interest chemists. The number of designs available for research on this kind of systems is not very large. This is because of two inherent problems associated with these systems. The first is that the mixture variables and the process variables have different characteristics. Specifically, mixture variables sum to one, whereas this does not hold for process variables. Stated otherwise, process variables can change without restriction whereas mixture variables cannot. In general, the variables can be grouped into two broad classes: The mixture variables are known as factors whose properties depend on the proportion of each component and not its absolute quantities. The quantity of each system component must be treated as a variable (variable of mixture), which is not independent of others (i.e., the sum of their proportions must be one). The mathematical terms can be described as follows [3]:

$$\sum_{i=1}^{q} x_i = 1, \quad 0 \le x_i \le 1 \tag{1}$$

where $q$ is the number of components of the mixture and $x_i$ are the components. Process variables are factors that are not part of the

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mixture, although when the levels are variable, they can affect the mixture properties. Process variables are independent and can change without restriction [3]. A straightforward combination of mixture variables and process design would be possible but for the second problem, that the number of design points tends to be very large. Therefore, a scheme is necessary that limits the number of design points [4]. Some papers reported the application of mixture and process variables [5–7].

One solution for reducing the number of experiments and thereby reducing the number of operational problems is to execute split-plot designs where the randomization requirement is relaxed [8]. Subsets of experiments of the complete design are carried out randomly in a number of randomized blocks. The easy-to-adjust factors are randomly varied within each block, whereas the hard-to manipulate factors are only randomly changed on passing from one block to another. More details in the case of split design can be found in Ref. [9]. As it has been stated in this paper, for unreplicated split design experiments, the whole plot and subplot errors are estimated using the restricted maximum likelihood (REML) approach by pooling the insignificant terms indicated by approximate normal probability plot [1]. Model accuracy can be verified by examining residual graphs and normal probability graphs of residuals.

Some types of catalysts in chemistry have interdependent composition and special structure. Spinel metal oxides are one of them which have attracted much attention for their remarkable catalytic properties, for example in catalytic combustion of volatile organic compounds. The compositions of spinel catalysts are interdependent and total mole fraction is considered to be 1. The composition and metal type used in spinel type catalysts affect the structure and activity of the catalyst. On other hand, the synthesis process of these catalysts is usually difficult. When using traditional methods, it is difficult to determine the combined influences of each component in the composite on the activity of catalysts, particularly the interaction effect between the components. Statistical strategies can provide facile and effective approaches to establish the quantitative relationship between dependent and independent variables [10–13].

The aims of this work were to optimize and to model the catalytic combustion of 2-propanol over $CuMn_mCo_{2-m}O_4$ spinel nano catalysts (m is the index of Mn in the formula). Since the preparation of spinel catalysts and catalytic study process were difficult, expensive and time consuming; therefore the unreplicated split design methodology was applied. We have obtained a quantitative equation describing the influence of the compositions of the precursors on the catalytic activity. The conversion of 2-propanol over catalysts was considered as response ($y$) of the model.

## 2. Experimental

### 2.1. Catalyst preparation

$CuMn_mCo_{2-m}O_4$ was synthesized using the sol–gel combustion method, as described in our previous work [14]. Stoichiometric amounts of nitrates were mixed in a minimum amount of demineralized water and the solution was heated at 60 °C for 1 h. Then in order to form the spinel phase, the samples were calcined. Since the ingredients of spinel catalysts are dependent on each other, the mixture design was used to determine the design of catalyst. According mixture constraint, the mole fractions of the ingredients present summed to 1.0. An equilateral triangle can be applied to represent the composition of the constituents in a tertiary system, with vertexes corresponding to the pure components and the points on and inside the boundaries representing the simultaneous occurrence of two and three components, respectively, in a system with no upper or lower limitations of each component. The three ingredients were copper ($x_1$), cobalt ($x_2$) and manganese ($x_3$) nitrates, whereas $x_1 + x_2 + x_3 = 1$ ($x$ = mole fraction).

Since in $CuMn_mCo_{2-m}O_4$ spinels, the mole of copper remain fixed ($x_1 = 0.33$), therefore the relation between $m$ and mole fraction will be as: $m = 2(0.67 - x_2)$. Two process variables which play an important role in the activity of catalysts are calcinations temperature ($z_1$) and reaction temperature ($z_2$); therefore, these variables were considered. Calcination temperature was adjusted at 700 °C (−1) and 800 °C (+1). In the case of reaction temperature, 200 °C and 300 °C were considered as low level and high levels of variable. All prepared samples were divided into two parts. The first samples were calcined at 700 °C and other parts were calcined at 800 °C for 6 h to ensure the absence of carbonaceous residues which may remain in the samples. Split-plot design of experiments and calculations were performed using the SAS/STAT software.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out on a SIEMENS D5000 X-ray powder diffractometer equipped with a Kristalloflex 760 X-ray generator with curved graphite monochromator which made possible the selection of the Cu $K_\alpha$ radiation (40 kV/30 mA). Infrared (IR) spectra were recorded with a Bruker 27 FT-IR spectrometer using the Universal ATR Accessory in the range from 3650 to 400 $cm^{-1}$ with 4 $cm^{-1}$ resolution. SEM characterization was carried out with a scanning electron microscope (model EQ-C1-1).

### 2.3. Catalytic study

Activity measurements of catalysts in combustion of 2-propanol, as a model molecule of oxygenated volatile organic compounds were carried out in a laboratory catalytic setup as shown in Fig. 1. The catalytic combustion reactions of 2-propanol were carried out under atmospheric pressure. The reactor placed inside an electric furnace controlled by a proportional–integral–derivative controller (PID). Catalyst (0.2 g) was placed over a plug of glass wool and a thermocouple was placed inside the catalyst bed. Packing of the catalyst was accomplished with mechanical vibration, and the two ends of the column were plugged with glass wool. Total flow rate through the reactor was set at 100 mL $min^{-1}$. The reaction products were analyzed using a Shimadzu 2010 gas chromatograph apparatus equipped to a flame inductivity detector (FID).

## 3. Results and discussions

All structures of $CuMn_mCo_{2-m}O_4$ catalysts were characterized by XRD. Fig. 2 shows the XRD patterns of $CuCo_2O_4$ ($m = 0$), $CuMnCoO_4$ ($m = 1$) and $CuMn_2O_4$ ($m = 2$) as representatives of $CuMn_mCo_{2-m}O_4$ catalysts. $CuMn_2O_4$ showed tetragonal crystal systems, while $CuCo_2O_4$ showed a cubic structure system. All catalysts present spinel structures as compared with structures of $CuCo_2O_4$ (JCPDS = 01-1155) and $CuMn_2O_4$ (JCPDS = 45-0505). XRD pattern of $CuMnCoO_4$ showed peaks around 18°, 31°, 36.5°, 38°, 44°, 54°, 58° and 64° indicating the formation of $CoCuMnO_4$ spinel [15].

In order to approve the formation of spinel structure, the FTIR analysis was carried out.

Fig. 3 shows the FTIR spectra of these samples. The formation of spinel structures in the catalysts was confirmed by these techniques. The spinel structure is known to be characterized by IR spectra in the region 700 to 400 $cm^{-1}$ [16]. Two bands were observed in this region corresponding to the stretching vibration of