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# Structural characteristics of selected metal oxides used for the catalytic pyrolysis of sunflower oil

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ABSTRACT

Structural features of metal oxides are the primary motives for utilizing them in a number of reactions and hence, investigation of catalyst structure–performance relationship is essential. This study deals with the morphological characterization of the catalysts used ($Co_3O_4$, $V_2O_5$ and ZnO) for the catalytic pyrolysis of sunflower oil for biofuel production. Also, the % organic liquid product (OLP) and fractional distillates obtained for different catalysts were analyzed. The best catalytic activity was observed with $V_2O_5$ and it was found to give higher OLP yield and gasoline like fraction. Scanning electron microscope (SEM) images of the catalysts were analyzed to determine the structural modifications of the catalysts during the reaction. The $Co_3O_4$ particles attained irregular shapes after use whereas marginal structural changes were observed for ZnO. The most fragile portion of the $V_2O_5$ particles was found to be partially eliminated upon use. FTIR analysis revealed the presence of aliphatic esters and derivatives of esters in the synthesized OLP and its gasoline fraction. The properties such as density, specific gravity, kinematic viscosity, flash point and higher heat value of the product were within the limits of ASTM D6751 (B100) standards.



## 1. Introduction

The use of renewable resources for fuel production is a critical strategy for mitigating greenhouse gas emissions and reducing petroleum consumption [1–3]. In recent times, catalytic pyrolysis is gaining importance as an alternative pathway for biofuel production. The advantages of catalytic pyrolysis include low operational cost, compatibility of the technology with available infrastructure, raw material flexibility, and production of IC engine compatible product [4]. The catalysts employed include metal oxides, molecular sieves, activated alumina and sodium carbonate. The selection of appropriate catalyst for the effective pyrolysis is very important. The studies pertaining to catalytic pyrolysis of vegetable oils indicated variations in product formation with catalyst type and reaction conditions. [5–8]. The use of catalysts reported to lower the reaction temperature and increase the conversion besides producing better quality product in a short reaction time [9]. The catalytic pyrolysis produces liquid hydrocarbons within the boiling point range of gasoline and kerosene [9]. Metal oxides find extensive applications in various catalytic processes due to their unique properties such as high specific surface area, strong base strength and high concentration of base sites [10,11]. It should be noted that these properties are related to the structural features of the metal oxides [12–15]. The hollow structure of cobalt oxide ($Co_3O_4$) plays a vital role in catalyzing a reaction. The catalytic activity of $V_2O_5$ in partial oxidation of hydrocarbons is due to the presence of vanadyl group (V=O), and its selectivity depends on the nature of the support, pretreatment conditions, and the mode of dispersion of vanadium on the support surface [16]. Zinc oxide is considered as an ideal catalyst for thermo-catalytic reactions as it contains both acidic and basic sites.

It is essential to identify the structure-performance relationships since it helps to improve the catalytic activity and to design better catalysts. The performance of metal oxide catalyst depends on a variety of parameters such as particle shape, catalyst surface structure, chemical bonding and interaction between the surfaces over layer/particle. It is evident that the structural characterization of catalysts in heterogeneous catalysis is inevitable [17–19]. The present study was carried out to analyze the structural modification of selected metal oxide catalysts used for the catalytic pyrolysis of sunflower oil, and to evaluate the effect of these catalysts on % OLP yield and fractional distillates.

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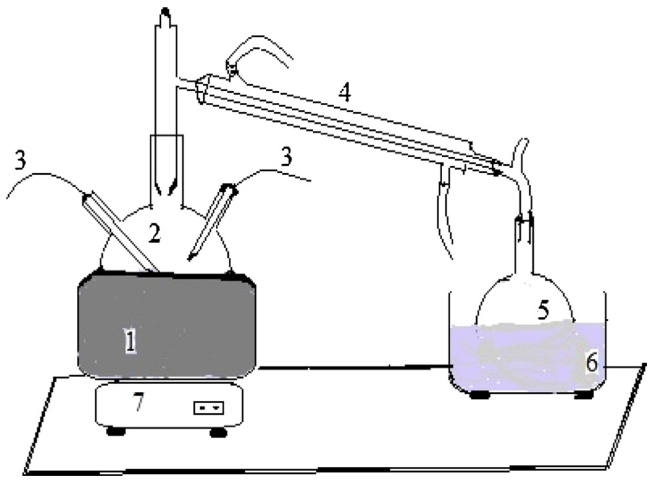


**Fig. 1.** Experimental setup: (1) Heating mantle (2) Three necked flask (3) Thermocouples (4) Condenser (5) Receiver (6) Ice bath and (7) Temperature controller.

## 2. Materials and methods

### 2.1. Materials

Sunflower oil of commercial grade was purchased from the local market and used without any further treatment. The fatty acid composition of the oil was found to be: oleic acid 58.4%; linoleic acid 23.5%; palmitic acid 9.3%; stearic acid 7.7%; and pentadecanoic acid 1.0%. The catalysts used in the current investigation ($Co_3O_4$, $V_2O_5$ and ZnO) and alumina ($\alpha$-$Al_2O_3$) were supplied by Fisher scientific (India). The alumina was used to reduce mass transfer limitations during the process by providing more surfaces for the catalyst to spread on. The catalytic cracking was carried using digital heating mantle and the temperature was controlled using digital temperature controller working in conjunction with two thermocouples with an accuracy of +/−2 °C.

### 2.2. Characterization of the catalysts

Surface structures of the catalysts before use were characterized using scanning electron microscope (SEM) (VEGA 3 TESCAN Czech Republic). The samples were mounted with double sided carbon tape on brass prior to the analysis for easy magnification. The fresh catalysts were also subjected to FTIR analysis (PerkinElmer Infrared model 337).

### 2.3. Cracking

The schematic diagram of the experimental setup is shown in Fig. 1. Catalytic pyrolysis was carried out in a 250 ml, three-necked, round bottom flask equipped with Liebig Drip Tip condenser fitted on the middle neck. Initially, about 0.5 g of alumina was transferred into the reactor. After the addition of appropriate amount of catalyst and oil, the reactor was placed on a heating mantle. The temperature of the mantle was set at 320 °C and the pyrolysis was carried out for 40 min. The catalyst concentration, pyrolysis temperature and residence time were arrived based on the previous study [20]. Thermocouples inserted through the respective side necks were used to measure the temperature of the reactants and vapor leaving the reactor. The condensate collected was placed in the ice bath for further cooling. The dark residue containing glycerol and catalyst were disaggregated in the oil and retained in the flask. The % OLP was calculated using the following equation:

$$\%\text{OLP yield} = \left(\frac{\text{Weight of OLP collected}}{\text{Weight of initial oil used}}\right) \times 100 \quad (1)$$

### 2.4. Analytical study

The catalyst precipitated in the reactor was calcinated in a furnace at 450 °C for 3 h. The glycerol was removed during calcination and the weight of the catalyst recovered was found to be equal to the weight of the catalyst initially added. The surface structures and FTIR spectra of the calcinated catalysts were recorded again. The properties such as density ($\rho$), specific gravity (SG), kinematic viscosity ($V$), higher heating value (HHV) and flash point (FP) of

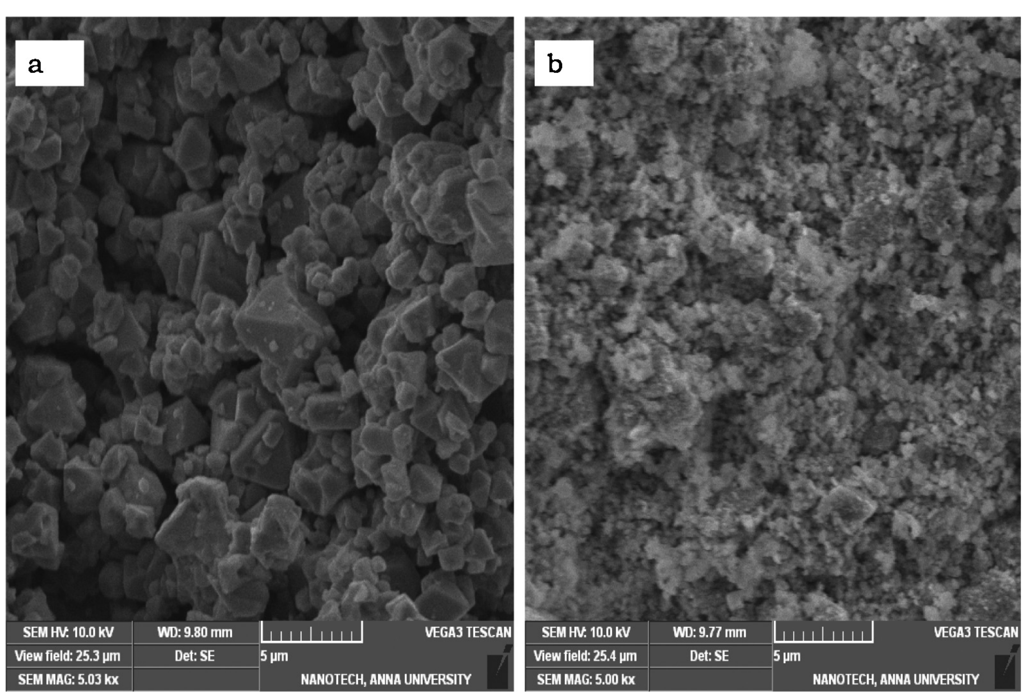


**Fig. 2.** Scanning electron micrographs (SEM) of $Co_3O_4$ (a) before reaction (b) after reaction (3000×).