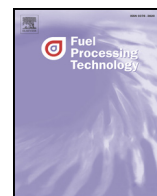




Contents lists available at ScienceDirect

## Fuel Processing Technology

journal homepage: [www.elsevier.com/locate/fuproc](http://www.elsevier.com/locate/fuproc)

Short communication

Effects of methanol co-feeding in ethanol synthesis from syngas using alkali-doped MoS<sub>2</sub> catalystsM.A. Portillo Crespo<sup>a</sup>, A.L. Villanueva Perales<sup>b,\*</sup>, F. Vidal-Barrero<sup>b</sup>, M. Campoy<sup>b</sup><sup>a</sup> Foundation Advanced Technological Centre for Renewable Energy (CTAER), Paraje Retamares, s/n. C.P. 04200 Tabernas, Almería, Spain<sup>b</sup> Bioenergy Group, Department of Chemical and Environmental Engineering, Escuela Técnica Superior de Ingeniería, University of Seville, Camino de los Descubrimientos s/n. 41092 Seville, Spain

## ARTICLE INFO

## Article history:

Received 5 December 2014

Received in revised form 3 February 2015

Accepted 7 February 2015

Available online xxxx

## Keywords:

Mixed alcohol synthesis

Bioethanol

Molybdenum sulfide

Syngas

Methanol co-feeding

## ABSTRACT

Gasification of biomass to syngas followed by catalytic conversion of syngas over mixed alcohol catalysts is an alternative pathway to produce bioethanol. Significant improvements in catalyst and process development need to be achieved to make this process commercially attractive. It is known that ethanol is produced from methanol by means of a CO insertion mechanism in the case of mixed alcohol MoS<sub>2</sub> catalysts. Thus, an improvement in the industrial process could be to recycle methanol produced in the reactor. This paper examines experimentally the influence of methanol co-feeding for a wide range of methanol concentration in the feed at different reaction temperatures. The results reveal that CO conversion and productivity of ethanol and higher alcohol increase linearly with methanol concentration in the feed for a given reaction temperature, while hydrocarbon productivity increases exponentially. Therefore, there is a trade-off between increasing alcohol productivity and the selective conversion of methanol to alcohols. When the concentration of methanol in the feed changes from 0% to 8% mole concentration, ethanol and higher alcohol productivity increase more than two-fold. The addition of methanol has a positive influence in the ethanol selectivity only at low methanol content in the feed.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Gasification of biomass to syngas, followed by catalytic conversion of synthesis gas to mixed alcohols is a promising route for the production of bioethanol [1]. Improvements in catalyst and process development need to be achieved to make the process commercially viable [2].

Santiesteban [3] carried out experiments with labeled methanol over an alkali/Co-MoS<sub>2</sub> catalyst and concluded that ethanol is produced from methanol through a CO insertion mechanism. This means that in an industrial process, methanol produced in the reactor could be recycled back to the reactor along with syngas to further increase ethanol production. The literature where methanol co-feeding is experimentally studied is very scarce. Gunturu [4] ran experiments, based on a fractional-factorial experimental design, in a Berty-type reactor to evaluate the kinetics of higher alcohol synthesis over an alkali/Co-MoS<sub>2</sub> catalyst. The variables considered were temperature (T), partial pressures of carbon monoxide (P<sub>CO</sub>), hydrogen (P<sub>H<sub>2</sub></sub>) and methanol mole concentration in the feed (C<sub>MET</sub>). The range of operating conditions was T: 300–350 °C, P<sub>CO</sub>: 14–28 bar, P<sub>H<sub>2</sub></sub>: 14–28 bar and C<sub>MET</sub> 0–4%. Results of this experimental design indicated that methanol co-feeding enhances CO conversion and the productivity of ethanol, higher alcohols and hydrocarbons. Quarderer et al. [5] reported significant improvement in higher alcohol productivity using a K/MoS<sub>2</sub> catalyst by

injecting methanol into the feed syngas. The conditions of the experiments were: 260 °C, 175 bar, GHSV: 1870 h<sup>-1</sup>, H<sub>2</sub>/CO: 1.12 and methanol feed rate (g/h) = 0–5.9–7. They also showed that adding ethanol improved higher alcohol productivity, however, the effect was not as pronounced as it was with methanol addition.

Experiments with methanol co-feeding may be of interest in order to generate a model which is able to predict how the catalyst may perform as a result of significant methanol recycle, and design a process that considers methanol recirculation. Very few kinetic models have been developed for alkali doped MoS<sub>2</sub> catalysts [7–10]. Of these, Gunturu examined the possibility of methanol recycle. The kinetic model by Gunturu was adopted as a starting point for the work of Larsson et al. [11], which slightly reformulated and refitted the parameters of Gunturu's model but also included the water–gas shift reaction. This kinetic model was validated against experimental data obtained from various literature sources with experiments that do not take the methanol recycle into account. However, Philips et al. used the same kinetic and reactor model as Larsson's to study by simulation the effect of methanol recycle at different temperatures [12]. NREL simulated a process for alcohol production with methanol recycle over promoted MoS<sub>2</sub> catalysts [6]. The reactor was modeled using a kinetic model supplied by The Dow Chemical under confidential agreement [14]. The model was developed by Dow Company using both bench-scale and pilot-scale data but this model has not been published in literature.

As previously mentioned, the literature has studied the effect of co-feeding methanol to MoS<sub>2</sub>-based mixed alcohol catalysts, but a more

\* Corresponding author. Tel.: +34 954487281; fax: +34 954461775.  
E-mail address: [angelluisvp@us.es](mailto:angelluisvp@us.es) (A.L. Villanueva Perales).

thorough assessment is necessary in order to determine to what extent ethanol productivity increases with high methanol concentration in the feed. Moreover, the effect of methanol addition should be assessed at different reaction temperatures, which significantly affect the rate of the reactions that take place over these types of catalysts. These experiments have been carried out and presented in this work. The results may also be of great value to obtain a kinetic model that reliably predicts the effect of methanol recycle, which is not available in the literature. This kinetic model could be used in the simulation of the whole mixed alcohol process in order to determine the optimum methanol recycle which results in the highest ethanol productivity. That model is currently being researched and will be published in the future.

## 2. Experimental setup

Fig. 1 shows a diagram of the experimental setup. Extremely pure CO, N<sub>2</sub> and H<sub>2</sub> and two mixtures of H<sub>2</sub>S and H<sub>2</sub> are supplied from pressurized cylinders. A mixture of 10% H<sub>2</sub>S in H<sub>2</sub> is used for the pretreatment of the catalyst, while a mixture of 400 ppm H<sub>2</sub>S in H<sub>2</sub> is used to maintain a 50 ppm H<sub>2</sub>S concentration in the feed gas to the reactor in order to maintain the activity (sulphidity) of the catalyst. The CO/H<sub>2</sub> mole ratio and total flow of the feed are adjusted with mass flow controllers. Before being fed to the reactor the gases pass through a carbonyl filter to prevent catalyst poisoning by Fe and Ni carbonyls. A HPLC pump has been used for methanol co-feeding tests. The experiments were carried out in a high pressure fixed bed reactor (inner diameter: 8.3 mm, length: 330 mm, stainless-steel). A bed of catalyst particles

(5 g) was placed inside the reactor supported with CSi. An alkali-doped MoS<sub>2</sub> catalyst produced by an industrial manufacturer based on a patented formulation was used [13]. Two spiral resistances supply heat to the reactor to maintain the reactor temperature, which is measured with a multipoint thermocouple type K located along the reactor. Downstream from the reactor, the pressure is maintained with a pressure control valve. The tube between the reactor and the gas chromatograph (GC) is wrapped in heat tracing tape to avoid condensation of liquid on the pipe. The temperature of the heat tracing is about 200 °C.

The reactor outlet stream is in vapor-phase and is analyzed on-line using a GC detection system (Agilent 7890 A) equipped with a thermal conductivity detector and two flame ionization detectors, which use helium as a carrier gas. Behind the GC, there is a condenser to separate the liquid and gaseous components. The condenser temperature varies between 0 to 10 °C depending on the inlet gas temperature and the room temperature.

With this experimental lab-scale setup, several tests were carried out in series at different temperatures (280, 290 and 300 °C) and molar concentrations of methanol in the feed (0, 2.98%, 4.68%, 5.79%, 8.44%) maintaining the pressure (110 bar), the H<sub>2</sub>/CO molar ratio (1) and GHSV (~1300 h<sup>-1</sup>) constant, in order to study the effect of methanol co-feeding. Each test lasted at least 12 hours to ensure that steady state was reached, resulting in 400 hours of operation for all tests. Prior to these tests, the catalyst was subjected to a sulphurisation and reduction pretreatment by feeding a mixture of H<sub>2</sub> and H<sub>2</sub>S (10% v/v). The pretreatment was comprised of two steps. First, a preheating from room temperature to 400 °C at 2 °C/min was carried out. Next, the

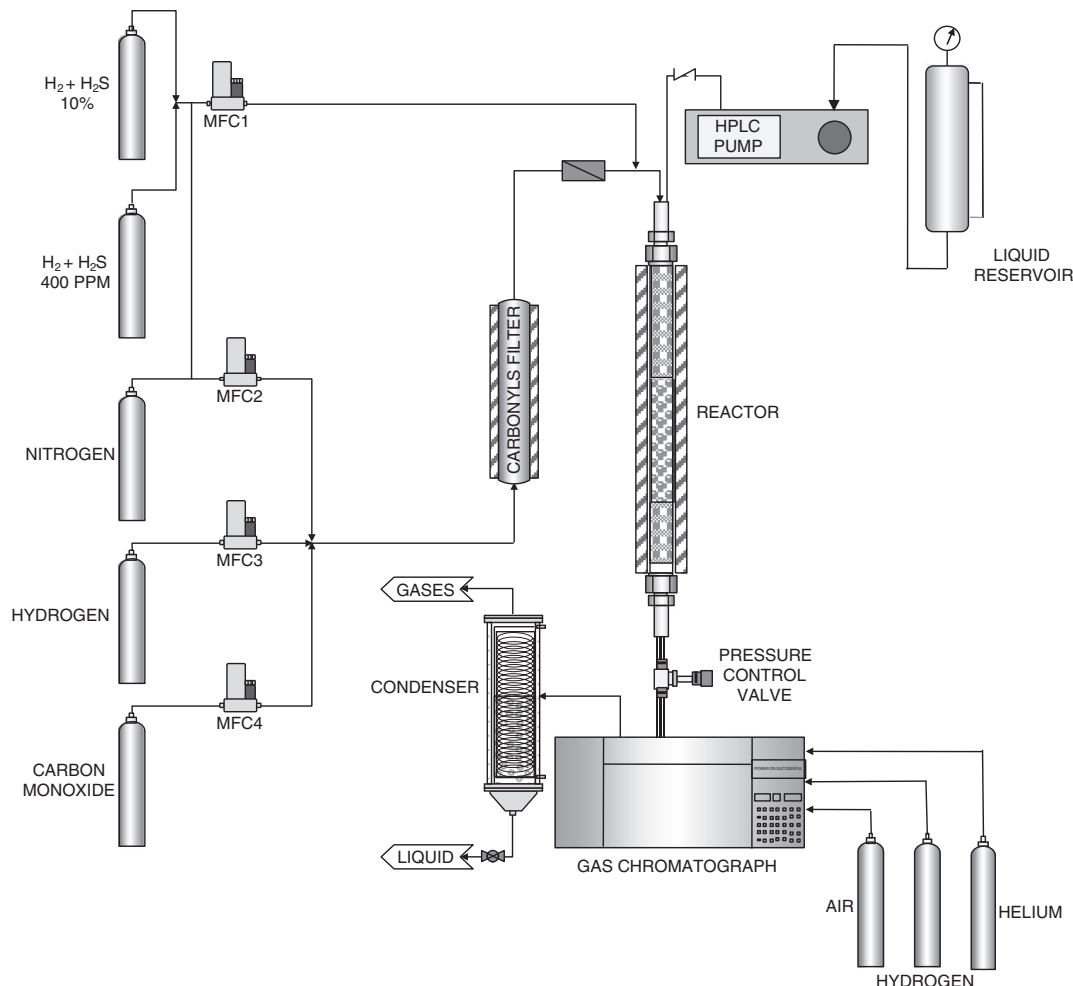


Fig. 1. Simplified diagram of the experimental setup.

Download English Version:

<https://daneshyari.com/en/article/6657053>

Download Persian Version:

<https://daneshyari.com/article/6657053>

[Daneshyari.com](https://daneshyari.com)