

Performance of a double-bed bench-scale catalytic reactor for acetone self-condensation to mesitylene: a renewable route to produce jet fuel additives.

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Highlights

- Mesitylene production from renewable acetone catalyzed by Al-MCM-41 and TiO₂.
- Commercial size of catalysts tested in bench-scale double-pipe reactor.
- Optimization of catalyst arrangement in double-bed to maximize mesitylene yield.

1. Introduction

The aviation industry is claimed to experience an important change in the following years and decades to reduce the emissions of greenhouse gases (GHG). In this context, sustainable production of jet fuel additives, like mesitylene, plays an essential role to decrease its carbon footprint. Nowadays, the main industrial production of mesitylene is as by-product of crude oil processing, specifically in cracking and reforming operations. The production of mesitylene by acetone self-condensation opens the possibility for an environmentally friendly route. Acetone has been proposed as a sustainable platform molecule to integrate the bio-refinery and production processes into a circular economy. The so-called ABE fermentation can produce acetone, butanol, and ethanol from biomass (e.g., agriculture waste) [1].

Acetone self-condensation to mesitylene is a multiple-step reaction process, based on a sequence of condensation and dehydration reaction stages, catalyzed by acid or basic solid catalysts. Basic catalysts promote the formation of phorone intermediates, while acid catalysts are able to accomplish the complete condensation to mesitylene. However, acid catalysts have some drawbacks, due to the formation of acetic acid and isobutene in a side reaction, which is also responsible of a fast initial catalyst deactivation [2]. The selection of a suitable catalyst, able to maximize mesitylene production with tolerance to deactivation, is the key to ensure the process viability. Previous works were focused on the development of suitable catalysts of this reaction [2-3]. It was found that acid and basic catalysts exhibit quite different behavior in terms of product selectivity, which is not optimum due to the formation of many side products. Al-MCM-41 and TiO₂, respectively, with acid and basic properties, have been selected as catalysts for this reaction. Both catalysts can operate within the same pressure (2.5 bar) and temperature range (250-300°C) with good activity [3].

In the present work, a bench-scale fixed-bed reactor was used to test the performance of these catalysts at commercial size. The behavior of the reactor is studied in either a single fixed-bed arrangement or two consecutive fixed-beds formed by a mechanical mixture of these catalysts. By this way, the advantages of both catalysts can be exploited.

2. Methods

The bench-scale reactor consists of a stainless-steel double-pipe with 500 mm length, 28 mm inside diameter of the inner tube, and 48 mm inside diameter of the outer tube. The catalysts pellets (3.2 mm diameter and 8 mm length) were placed inside the inner tube as a single or double fixed bed. The gas feed consisted of a mixture of vaporized acetone and nitrogen with flow rates controlled, respectively, using a HPLC pump and a mass flow controller. Different space velocities were tested by adjusting total gas flow rate and catalyst loading in the reactor. The temperature of the reactor was measured and controlled using a thermal liquid flowing through the annulus section of the double-pipe reactor. The temperature of this liquid was regulated using an electrically heated recirculating bath. The double-pipe reactor was surrounded by insulating material to reduce heat losses. The reactor effluent was analyzed using a gas chromatograph (AGILENT HP-6890 N).

3. Results and discussion

The experiments with the bench-scale reactor have been done at 275°C, 280 kPa and with a gas feed made of 10% acetone on nitrogen. It was found that the reactor operated at quasi-isothermal conditions thanks to the use of a thermal fluid to extract the heat of reaction. This fluid was introduced at high rate through the annulus section of the double pipe. The total gas flow rate was varied in the range 0.72 to 10.8 mol/h, depending on the catalyst and bed arrangement, to obtain different reactor space velocities (WHSV is the ratio of total gas flow rate to total catalyst weight).

A stabilization period, in which conversion decreased, was observed with fresh catalysts for around 5 h. Then, conversion was constant upon time for all the catalysts and bed arrangements. The results presented in Fig. 1 correspond to the performance after the stabilization period. Conversion decreased on increasing WHSV for all the catalysts, since the reaction contact time decreased (Fig 1a). The single-bed TiO₂ catalyst exhibited higher conversion than the Al-MCM-41 one. The product distribution of these two catalysts was quite different (Fig 1b): the main product was isophorone with TiO₂ and mesitylene with Al-MCM-41. However, the latter catalyst was responsible for the generation of undesired isobutylene by decomposition of methyl oxide, an intermediate of acetone self-condensation reaction. Therefore, it was explored the use of double-bed arrangements: the first bed of TiO₂ was aimed at converting acetone to mesityl oxide and isophorone, while the second bed of Al-MCM-41 completed the reaction to mesitylene. Of the two double-bed arrangements considered, the one with 2/3 of the bed (67 wt. %) made of Al-MCM-41 resulted in a better performance (Fig 1b). In this case, mesitylene yield increased considerably with respect to the TiO₂ single bed, while the formation of isobutylene was very limited. The conversion achieved by the double-bed arrangements for the different tested WHSV was in-between the corresponding single-bed catalysts (Fig 1a).

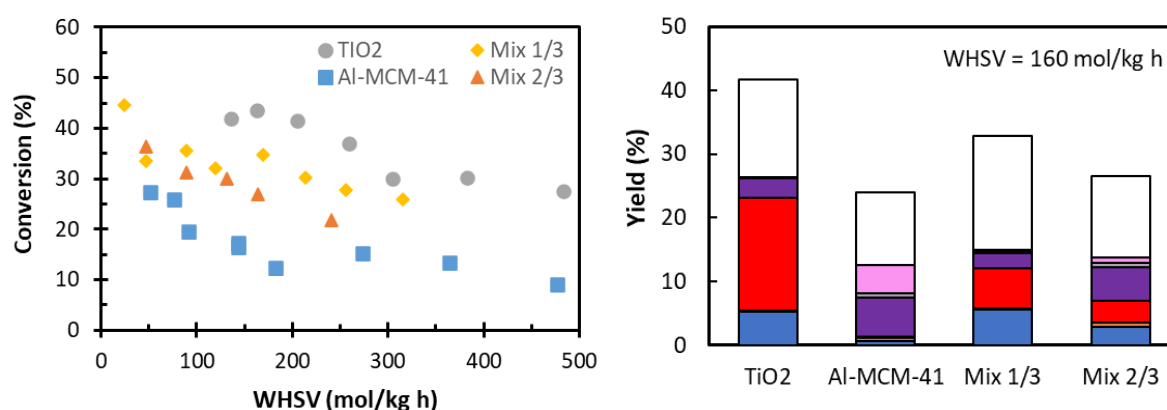


Figure 1. Performance of the different bed arrangements (single-bed TiO₂ and Al-MCM-41, and double-bed mixture with 1/3 and 2/3 of Al-MCM-41): (a) conversion and (b) product yield at 160 mol/kg h. Conditions: 275°C, 280 kPa, 10% acetone. (bar legend: ■ mesityl oxide, ■ isophorone, ■ phorone, ■ mesitylene, ■ isobutylene, ■ acetic acid, □ carbon balance)

4. Conclusions

Production of mesitylene by self-condensation of renewable acetone was demonstrated in a quasi-isothermal bench-scale double-pipe reactor, equipped with commercial-size catalysts. The double-bed arrangement, made of 1/3 TiO₂ and 2/3 Al-MCM-41 catalysts, resulted in high mesitylene yield without significant formation of undesired isobutylene. The information gathered with the bench-scale reactor can be used for the scale-up of the process.

References

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Keywords

Fuel additive; acid/base catalysis; bench-scale reactor; reactor optimization.