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Experimental Campaign for Methanol Synthesis with CO_2-rich Streams

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Highlights

- Valorization of whey waste from cheese industry
- Methanol production from hydrogen and carbon dioxide
- Comparison study of CZA catalysts performance

1. Introduction

Even though the technology to produce methanol (MeOH) from syngas (H_2/CO) is established, its application to new processes is challenging and worthy of new researches. In Italy, cheese industry produces 9.5 Mt of cheese whey (rich in lactose) which is recycled in swine farms or biogas plants. A fifth of this whey is wasted and the valorization of the rest as high-value food integrators is insufficient. A new way to enhance the cheese whey consists in an innovative bio-technological approach: the use of lactose as a platform for new chemicals. The fermentation of this waste-stream produces valuable gas stream (H_2/CO_2), a feedstock that is then transformed into new bio-based solvents and fuels (MeOH, DME). Methanol is one of the most important building blocks in the chemical industry with an annual production of about 90 Mt. It is used for the synthesis of several chemicals (MTBE, DME, acetic acid) and end-use products like plastics resins, gasoline additives, olefins, solvents and fuels. Today, methanol is synthetized from syngas (H_2/CO) with a catalyst CZA (Cu/ZnO/Al_2O_3) and operative conditions of 200-300 °C and 50-100 bar [1]. Here, we studied the performance and the feasibility of traditional CZA catalyst for methanol synthesis using CO_2 rich feed.

2. Methods

The experimental data were collected using a tubular fixed bed reactor charged with 1 g of catalyst. The flowsheet of the plant is reported in figure 1. We evaluated the influence of temperature (from 250 °C to 290 °C), pressure (from 15 bar to 25 bar) and feed composition (varying the ratio between H_2, CO_2 and CO). Hydrogen activated the catalyst inside the reactor for 3 hours at 300 °C and 5 bar. A GC analyzed the product condensed while an online uGC the gases. The CZA catalyst was prepared by co-precipitation of metal nitrate precursors [2]. BET, SEM-EDX, TEM, XRD, TPR analysis characterized the catalysts.

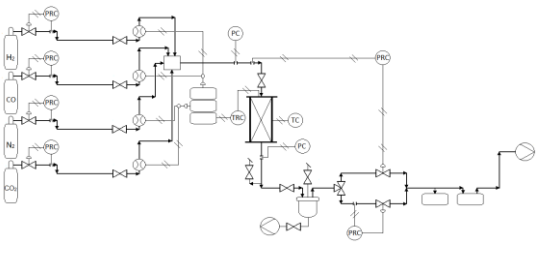

Figure 1. Plant flowsheet.

3. Results and discussion

XRD shows only the presence of CuO, ZnO and Al_2O_3 with a good dispersion. The surface area of our catalyst is about 20 m^2/g while the commercial one has a value of 91 m^2/g [4]. CO conversion, yield of the main fractions (CO_2, ethylene, isobutane and MeOH) and the amount of MeOH recovered at the end of the run are reported in Table 1. Higher the temperature, higher the CO conversion and the MeOH production.

T (°C)	CO conv. (%)	Yield (%)				Cold trap	
		CO_2	Ethylene	Isobutane	Methanol	Mass (g)	$\%_{Methanol}$
250	12,7	0,75	0	1,5	1,5	2,07	71,9
270	13,7	1,3	0,1	2,2	2,8	2,78	72,6

Table 1. Experimental results for temperature dependence tests (P=20 bar).

Increasing the pressure, the CO conversion increase, except for 20 bar probably due to experimental issue (Table 2). CO_2 and MeOH yields increase increasing the pressure, but ethylene and isobutane yields decrease.

P (bar)	CO conv. (%)	Yield (%)				Cold trap	
		CO_2	Ethylene	Isobutane	Methanol	Mass (g)	$\%_{Methanol}$
15	13,7	0,3	0,11	2,0	0,8	0,62	50
20	12,7	0,9	0	2,1	2,1	2,1	72
25	15,2	0,9	0	1,4	2,9	3,15	75

Table 2. Experimental results for pressure dependence tests (T=250 °C).

Increasing the CO_2 content, the quantity of liquid fraction produced decreases (Table 3) as the methanol fraction (from 71.8 % to 6.2 %). Using as feed H_2/CO_2 (without CO) the CO_2 conversion increases increasing the ratio but the liquid product is mainly water, with only 3.2 % of methanol.

H_2:CO:CO_2	CO conv. (%)	Cold trap	
		Mass (g)	$\%_{Methanol}$
16:8:0	17,3	2,07	71,8
16:8:1	12,4	0,69	66,9
16:8:2	11,4	0.39	6.2
16:8:4	10,8		

Table 3. Experimental results using syngas with different CO_2 composition (T=250 °C, P=20 bar).

Finally, a comparison between home-made CZA and commercial one was performed using as feed syngas. Results shows (Table 4) that using commercial catalyst it's possible increase the CO conversion and significantly improve the methanol quantity.

Catalyst	CO conv. (%)	Yield (%)				Cold trap	
		CO_2	Ethylene	Isobutane	Methanol	Mass (g)	%
Synthesized	12,7	0,8	0	1,5	1,5	2,07	71,9
Commercial	15,8	0,6	0,1	1,5	5,6	8,69	75,8

Table 4. Experimental results comparison between commercial an synthetized catalyst (T=250 °C, P=20 bar).

4. Conclusions

Traditional CZA catalyst could be used for methanol production using syngas with low percentage of CO_2 but methanol selectivity is lower compared with pure syngas. This, probably, is due to Reverse Water Gas Shift reaction, also catalyzed by copper, that consume H_2 and CO_2 producing H_2O and CO. New study should be done increasing the severity of operating conditions and considering promotes like zirconium oxide or more specific catalysts able to increase the CO_2 conversion to methanol.

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References

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Keywords
CO2-rich gas, Methanol, CZA, Waste valorization