MIXED ALCOHOL RENEWABLE GAS (MARG) PROCESS - LABORATORY TRIALS

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Abstract

The catalytic conversion of synthesis gas (syngas) from biomass gasification to mixed alcohols (C_1-C_5) and renewable natural gas (RNG) over alkali-doped molybdenum sulfide (MoS_2) catalysts, a potential pathway of producing fuels and chemicals, was investigated to evaluate the effects by temperature, pressure, gas composition, and methanol recycle. To determine the effects of these parameters on mixed alcohol synthesis (MAS) and RNG production and composition, total four parameters were evaluated on a bench-scale MAS system, with variations in temperature, pressure, syngas-mixture composition, and amount of methanol injection. The bench-scale MAS system uses Alkali-promoted MoS_2-based catalyst which show various characteristics: high coke resistance, sulfur tolerance, high selectivity to higher alcohols, and high water-gas shift activity. These advantages make them suitable for syngas derived from biomass, which typically has a low H_2/CO ratio and moderate sulfur content. Three different gas compositions, including a reference gas for nominal gasifier composition from the West Biofuels Fast Internally Circulating Fluidized Bed (FICFB) and two other gases to simulate the effect of recycling CO_2 and tail gas, were used in the tests. Three different operating temperatures (270°C, 300°C, and 330°C) as well as three different operating pressures (60bar, 80bar, and 100bar) were performed. Methanol-injection experiments were conducted to simulate and evaluate the process of recycling separated-methanol from product stream to increase the efficiency of the MAS and RNG production. The input gas composition is known while the output tail gas and liquid were analyzed using micro gas chromatography (GC) with TCD detector and a GC with an FID detector, respectively. Tests on the bench-scale MAS system were conducted to evaluate operational parameters to guide the future operation of the West Biofuels pilot-scale MAS/RNG facility.

INTRODUCTION

The conversion of syngas to mixed alcohols and RNG via mixed alcohol synthesis (MAS) using a molybdenum sulfide (MoS_2) catalyst is mainly affected by temperature, pressure, and syngas composition. To optimize operation conditions for a pilot-scale MAS system, using a slip-stream of producer gas from a pilot-scale fast internally circulating fluidized bed (FICFB) biomass gasifier as feed-gas, the following experiments were conducted, using a bench-scale MAS system.

Fig.1: Pilot-scale FICFB Gasifier at West Biofuels

Fig.2: Pilot-scale MAS system at West Biofuels

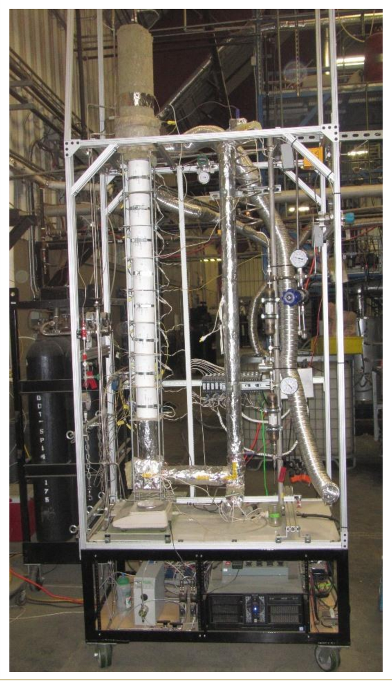


Fig.3: Bench-scale MAS system at West Biofuels

EXPERIMENTAL

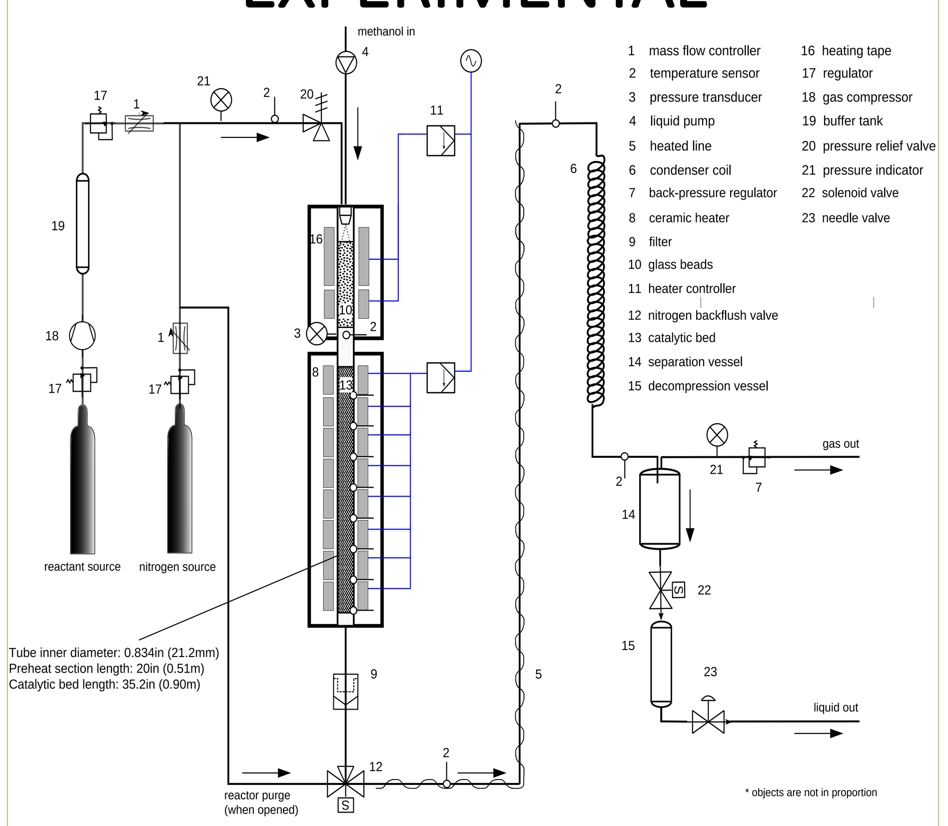


Fig.4 (above): Schematic of components in the Bench-Scale MAS system

Table 1: Design parameter of the Bench-Scale MAS system

Pressure	50 - 120	bar
Temperature	250 - 400	°C
Catalyst Volume	0.35	Liter
Producer Gas Flow Rate	0.1 - 10	slm
Gas Space Velocity	500 - 2000	1/h
Liquid Flow Rate	0.01 - 20	ml/min
Liquid Space Velocity	0.2 - 4	1/h

Parameter	Mixture	Temperature °C	Pressure bar	GHSV 1/hr	MeOH g/min
Temperature	B	270	100	1000	-
	B	300	100	1000	-
	B	330	100	1000	-
Mixture (Low temp)	B	270	100	1000	-
	E	270	100	1000	-
	F	270	100	1000	-
Mixture (High temp)	B	300	100	1000	-
	E	300	100	1000	-
	F	300	100	1000	-
Pressure	B	270	60	1000	-
	B	270	80	1000	-
	B	270	100	1000	-
Methanol (Low temp)	E	270	100	1000	0
	E	270	100	1000	7
Methanol (High temp)	E	300	100	1000	0
	E	300	100	1000	7

Table 2: Test Parameters

		B	E	F
		Woodland Specialty gas	With CO2 recycle	With 75% tail gas recycle (after alcohol removal)
		[vol%]	[vol%]	[vol%]
H2	Hydrogen	39.47%	34.53%	22.27%
CO	Carbon Monoxide	29.00%	25.38%	22.90%
CO2	Carbon Dioxide	20.00%	30.00%	35.00%
CH4	Methane	9.00%	7.88%	18.21%
C2H4	Ethylene	2.20%	1.93%	0.300%
C2H6	Ethane	0.32%	0.28%	1.305%
H2S	Hydrogen Sulfide	0.015%	0.013%	0.015%
Sum		100.00%	100.00%	100.00%
H2:CO ratio		1.36	1.36	0.97

Table 3: Gas Mixtures Composition

Low H_2/CO ration (<2.0)

Alcohol formation: $2n\ H_2 + n\ CO \rightarrow C_nH_{2n+1}OH + (n-1)\ H_2O$

Stoichiometric conversion of CO requires $H_2/CO = 2$

Methane formation: $3\ H_2 + CO \rightarrow CH_4 + H_2O$

Stoichiometric conversion of CO requires $H_2/CO = 3$

With Water-Gas Shift (WGS) (MoS_2-based catalysts):

WGS: $(n-1)\ H_2O + (n-1)\ CO \rightarrow (n-1)\ H_2 + (n-1)\ CO_2$

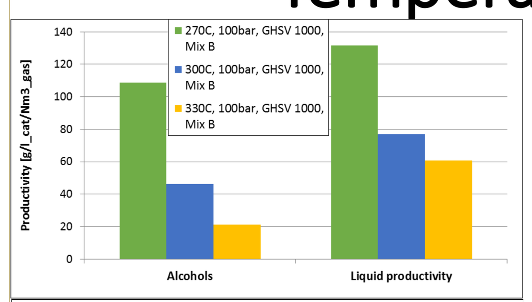
Alcohol net: $(n+1)\ H_2 + (2n-1)\ CO \rightarrow C_nH_{2n+1}OH + (n-1)\ CO_2$

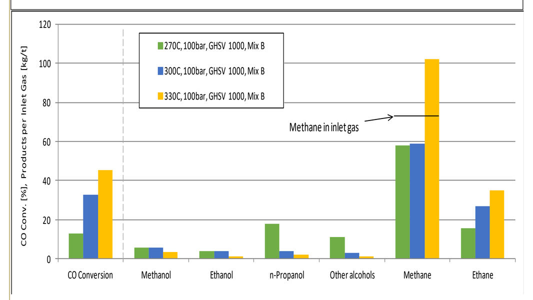
Stoichiometric conversion of CO requires $H_2/CO \leq 2$

Methane net: $2\ H_2 + 2\ CO \rightarrow CH_4 + CO_2$; $H_2/CO = 1$

RESULTS & DISCUSSION

Temperature

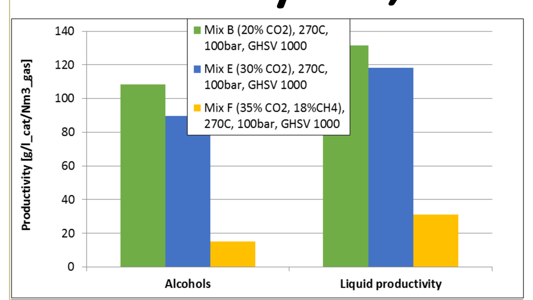


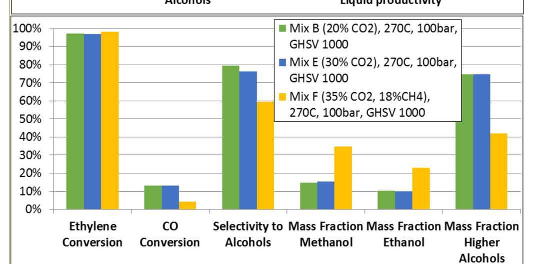


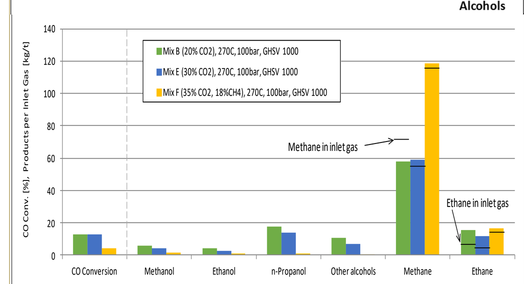
Higher temperature:

- Increase:
  - CO conversion
  - Production of methane and ethane
- Decrease:
  - Production of alcohols
  - Productivity of higher alcohols

Recycle, Lower Temp





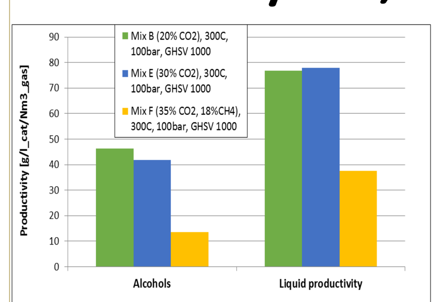


Alcohols production decreased when simulating recycle:

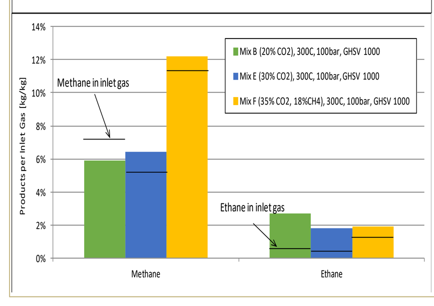
- Increase CO_2 and CH_4
- Decrease H_2/CO ratio
- Decrease ethylene (i.e. propanol)

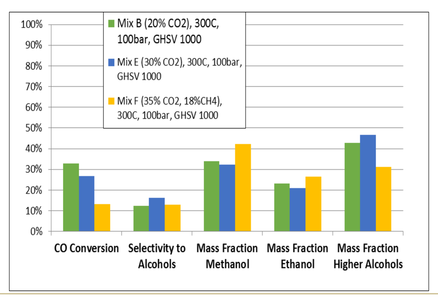
RNG production increased when simulating recycle

Recycle, Higher Temp



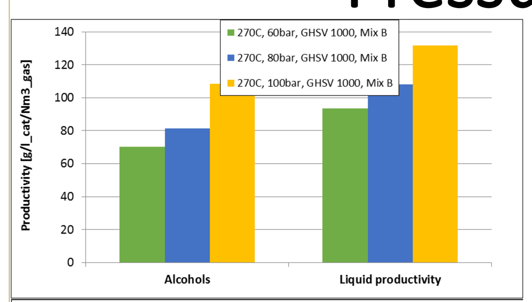
Agree with two above cases

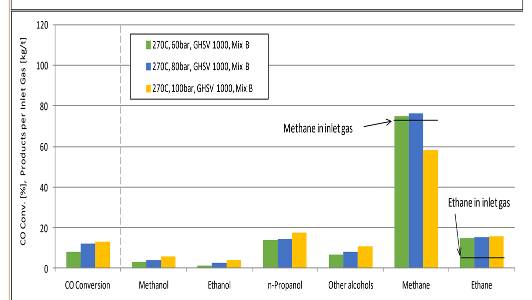




RESULTS & DISCUSSION

Pressure

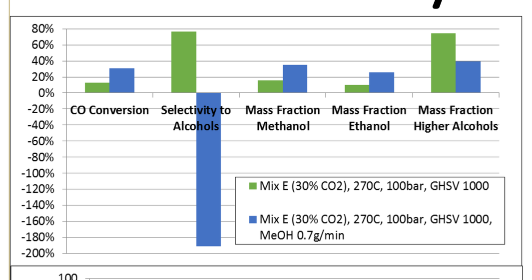


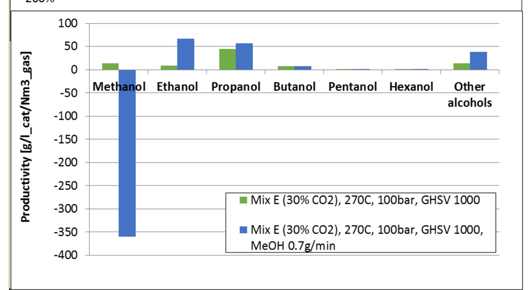


Higher pressure:

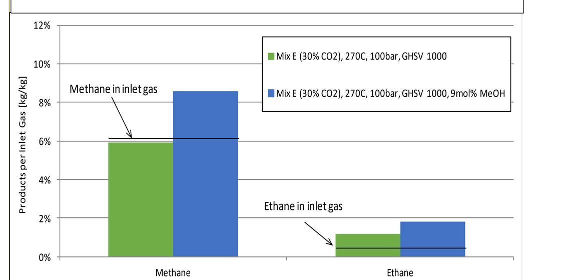
- Increase:
  - CO conversion
  - Production of alcohols
- Decrease:
  - Production of methane

Methanol Recycle, Lower Temp

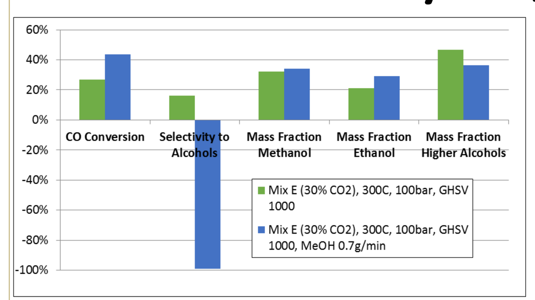




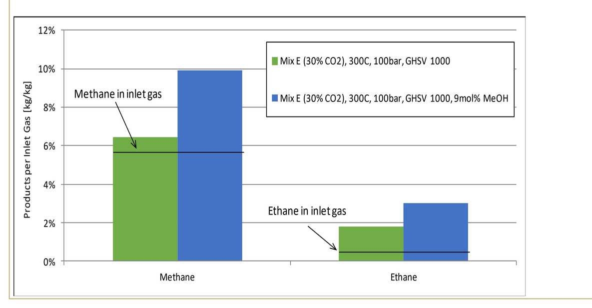
- Increase CO conversion
- Increase ethanol and propanol production
- Increase methane and ethane production



Methanol Recycle, Higher Temp



Agree with two cases: Temperature and Methanol Recycle @ lower temp



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