Glycerol as a Source of Fuels and Chemicals by Low-Temperature Catalytic Processing

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ACIEE, **2006**, *45*, 3982-3985

Alternative Fuels

- Ethanol (Methanol)
  - Currently replacing MTBE as a fuels oxygenator.
  - Questions remain concerning the long-term viability as a fuel.
  - Production and purification is energy intensive (fermentation/distillation).
  - Currently derived from food (grains, sugar cane, etc.)

- Bio-Diesel
  - Works in current distribution/ combustion systems.
  - Derived from seed oils (food).

- Hydrogen
  - Clean burning.
  - There is currently no economical method for hydrogen generation.
  - Distribution and storage?
  - Safety?

Biomass as a source of fuels? Current Strategies

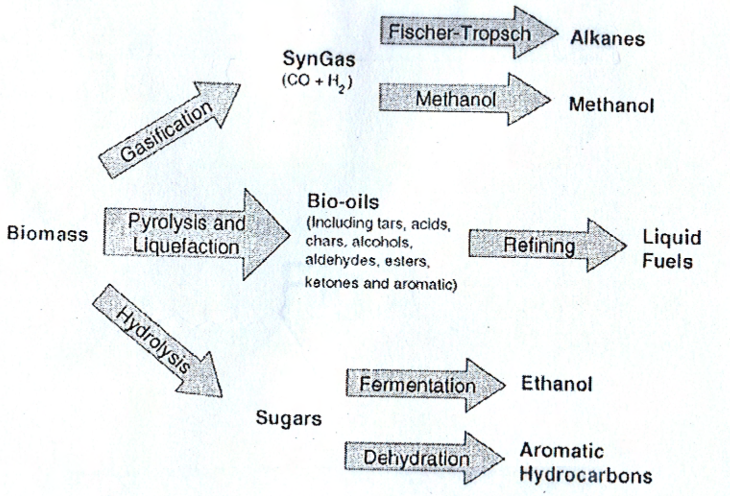
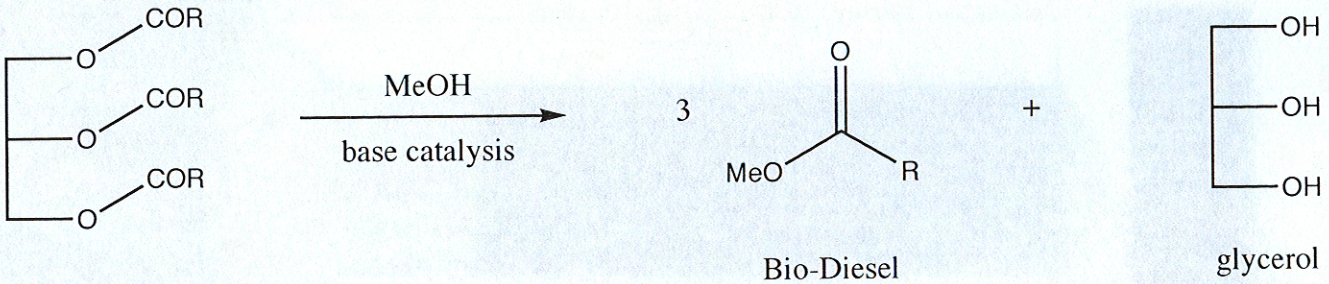


Fig. 3. Current strategies for production of liquid fuels from biomass.

Huber and Dumesic, Catalysis Today **2006**, *111*, 119-132

Bio-Diesel



triglycerides
from vegetable oils

What to do with all that glycerol?

conversion to synthesis gas:

$C_3O_3H_8 \rightarrow 3\,CO + 4\,H_2$ + 350 kJ/ mol

Fischer-Tropsch:

$8\,CO + 18\,H_2 \rightarrow C_8H_{18} + 8\,H_2O$ - 412 kJ/ mol

Overall:

$C_3O_3H_8 \rightarrow 7/25\,C_8H_{18} + 19/25\,CO_2 + 37/25\,H_2O$ - 63 kJ/ mol

Table 1: Experimental data for catalytic processing of glycerol into synthesis gas under various conditions.

Conditions		Conversion into gas phase [%]	H_2-TOF [min^{-1}]	H_2/CO	CO/CO_2	CH_4/H_2
Feed flow rate [cm^3 min^{-1}][a]	0.08	68	111	1.6	5.7	0.038
	0.16	71	241	1.4	8.8	0.036
	0.32	64	373	1.3	12	0.045
	0.64	39	449	1.3	17	0.038
Glycerol concentration [wt%][b]	20	64	265	1.4	8.7	0.025
	30[c]	50	285	1.3	14	0.032
	50	26	267	1.2	37	0.050
T [K][d]	573	17	104	1.31	90	0.037
	623	54	335	1.31	17	0.027
	673	100	600	1.33	11	0.027
	673[e]	72	450	1.38	–	–
	723	61	419	1.68	4.6	0.019
	723[e]	43	300	1.83	–	–

For these studies of reaction kinetics, 0.060 g of 5 wt% Pt/C was used. [a] Glycerol feed 30 wt%, 623 K, 1 bar. [b] Feed flow rate 0.32 cm^3 min^{-1}, 623 K, 1 bar. [c] Point taken after 2 h time-on-stream. [d] Glycerol feed 30 wt%, 0.32 cm^3 min^{-1}, 1 bar. [e] Point taken after 3 h time-on-stream.

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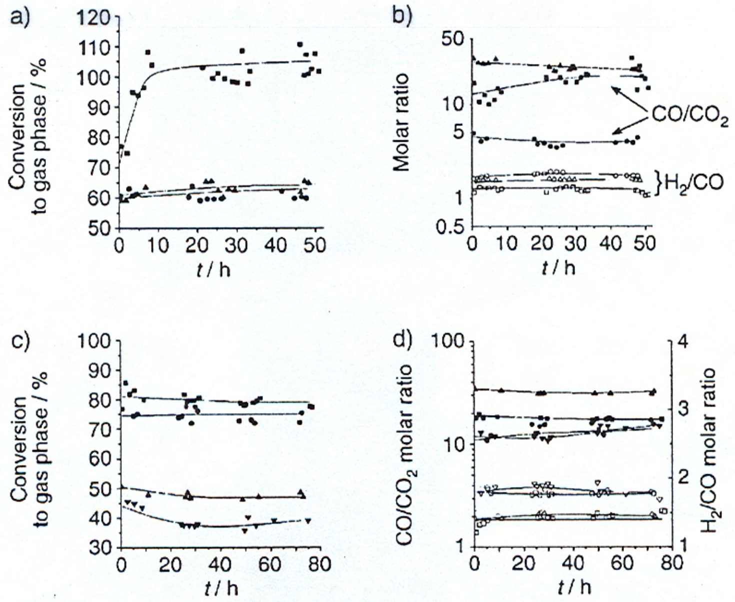

Figure 2. Performance of carbon-supported Pt and Pt-bimetallic catalysts under various process conditions. Variation with time-on-stream of a) percentage glycerol conversion to gas-phase products and b) molar ratios for conversion of 30 wt% glycerol at 1 bar (■), 50 wt% at 1 bar (▲), and 30 wt% at 20 bar (●) over 0.090 g Pt/C at 623 K. Variation with time-on-stream of c) percentage glycerol conversion to gas-phase products and d) CO/CO_2 (filled symbols) and H_2/CO (empty symbols) molar ratios for conversion of 30 wt% glycerol at 1 bar over Pt–Ru/C at 548 K (triangles; 0.435 g catalyst) and 573 K (squares; 0.513 g catalyst) and over Pt–Re/C at 498 K (inverted triangles; 0.535 g catalyst) and 523 K (circles; 0.535 g catalyst). A feed rate of 0.16 $cm^3\,min^{-1}$ for a) and b) and 0.08 $cm^3\,min^{-1}$ for c) and d) was used.

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Conversion of Glycerol to SynGas

- Pt-based catalysts are especially selective for C-C bond cleavage vs C-O bond cleavage.
- Water-Gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) needs to be suppressed or controlled.
- Bimetallic catalyst (Pt-Ru and Pt-Re) give moderate to good conversions of glycerol to synthesis gas at temperature suitable for the F-T reactions (Fe and Co based catalysts).

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Fischer-Tropsch Reaction: a brief history

$(CO + H_2 \rightarrow C_mH_n + H_2O)$

- 1925 to 1945: developed in Germany for the industrial production of fuels (600,000 t/ yr).

- 1945 to 1955: Further research into F-T occurred globally until the discovery and development of massive petroleum fields (Middle East, Alaska, North Sea, etc.)

- 1955 to 1970: Little interest in F-T processes.

- Embargos imposed on South Africa (1980's) lead to intensive development of F-T reaction to supply fuel and chemicals from coal and natural gas.

- Sasol is the world leader in F-T technology and produces 40% of the liquid fuels (gasoline, diesel and jet fuel) used in South Africa.

- Current capital investments focus on gas to liquid (GTL) F-T. Sites are operational in South Africa, Malaysia (15,000 b/d), Qatar with more sites planned.

- F-T offers significant potential for:
  - "clean coal technology" (Coal reserves are estimated to be 20 times that of crude oil)
  - exploiting "stranded gas reserves"

C & EN, June 5, 2006, p 57-61.
Dry, M. E. Applied Catalysis A: General **2004**, *276*, 1-3.
Schulz, H. Applied Catalysis A: General **1994**, *186*, 3-12.
BusinessWeek Online, February 27, 2006.
Sasol company brochure (www.sasol.com).

Fischer-Tropsch Reaction

$(CO + H_2 \rightarrow C_mH_n + H_2O)$

- Fe and Co are most common catalysts (Ni gives mainly CH_4; Ru gives high MW products)

- High temperature F-T (HTFT)
  - 340 °C
  - Fe catalyst
  - Olefins and gasoline (unbranched, so low octane rating)

- Low temperature F-T (LTFT)
  - 230 °C
  - Fe or Co catalysts
  - High quality Diesel (free of Sulfur and Nitrogen) and linear waxes (can be hydrocracked to diesel/ jet fuel)

Direct Conversion to Hydrocarbons

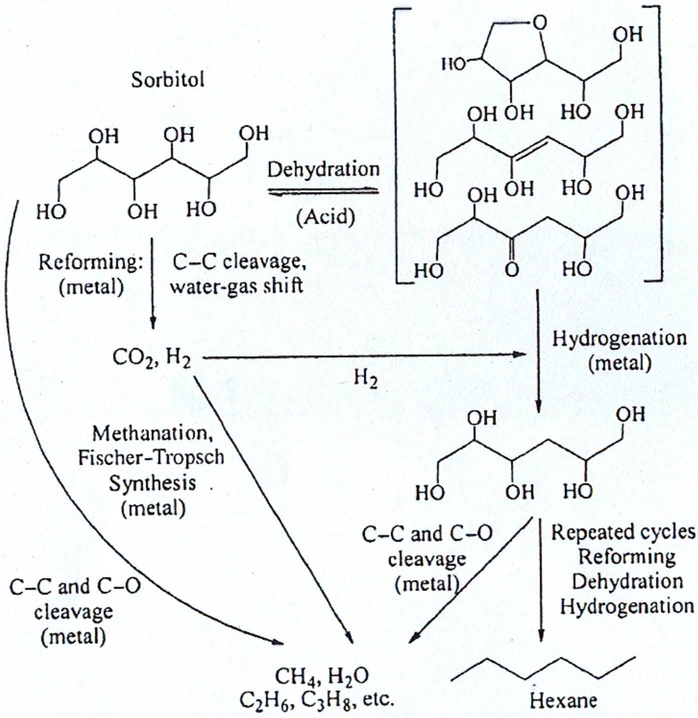

Figure 1. Reaction pathways for the production of alkanes from sorbitol in aqueous solution over a $Pt/SiO_2/Al_2O_3$ catalyst.[10]

Angew. Chem. Int. Ed. **2006**, *45*, 696–698

ACIEE **2006**, *45*, 696-698.

Conclusions

- Conversion of biomass (glycerol) to synthesis gas using metal catalysts in aqueous systems was demonstrated.
- Mixed metal systems showed best results.
- Conversion of biomass directly to hydrocarbons was also demonstrated, but requires a hydrogen cofeed for best results.
- Aqueous phase reforming of biomass to synthesis gas cannot compete with the conversion of natural gas to liquid hydrocarbons (GTL) technology.
- Aqueous phase reforming of biomass will likely have niche applications for the conversion of waste streams to more valuable products (ethanol/ biodiesel industry).