Alkylation of Alkanes: More Efficient Use of Carbon Feedstocks through Tandem Catalysis

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Renewable and Sustainable Fuel Solutions for the 21st Century

A NSF IGERT Project at Rutgers University

Introduction: The Transportation Fuel Problem

US Oil Consumption and Limited Reserves

U.S. OIL

consume: 7 billion barrel/yr
reserves: 22 billion barrel
import: 60% of consumption: \$300B/yr (+ "other" costs)

But, vast reserves of non-petroleum fossil fuels:

ENERGY RESERVES (Quads)*

	Oil	Gas	Coal	Shale
US	130	183	5700	6400
world	7400	6100	21000	9200

Biomass: 100(?) Quads/year

***U.S. TOTAL ENERGY consumption: 100 Quads/year**

(Most potential alternatives will produce electricity, not transportation fuel.)

Fischer-Tropsch Diesel

"Dieselization [moving from gasoline to diesel] will ultimately lead to *cleaner* air."

-James J. Eberhardt, U.S. Department of Energy

- Europe: majority of cars now diesel (vs. 20% in 1992)

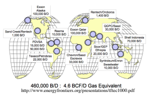
Fischer-Tropsch Diesel (FT diesel; clean diesel)

- approx. 30% more efficient (mpg and miles per CO_2) than gasoline
- "ultra-clean": extremely low (0-5 ppm) sulfur, aromatics, and toxics
- could replace 100% of transportation fuel supply

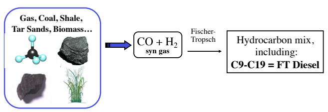
replacing conventional diesel (currently 22%) with FTD will have the biggest effect on air quality (especially for particulates)

Many FT(gas) plants in operation overseas and more are currently being built.

South Africa runs primarily on FT diesel from **coal.**



Fischer-Tropsch Chemistry for Energy Security



Coal reserves: all US energy needs for 50+ years

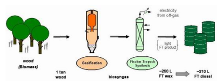
Oil-shale: all US energy needs for 50++ years

Biomass: forever …sustainable supply of biomass sufficient to displace 30 percent or more of the country's present petroleum consumption – with relatively modest changes in land use …. should not be thought of as an upper limit….

http://www.eia.doe.gov

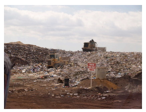
DOE/USDA joint report, April, 2005 http://www1.eere.energy.gov/biomass/pdfs/final_billionton_vision_report2.pdf

Fischer-Tropsch Feedstocks Beyond Coal

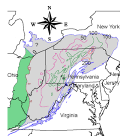


http://www.bioenergy-noe.org/?_id=156

http://www.chrisgas.com



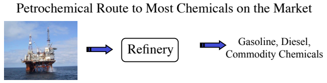
Municipal waste for gasification



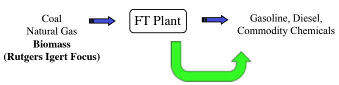
Shale gas

Fischer-Tropsch vs Petrochemical Processes

Petrochemical Route to Most Chemicals on the Market

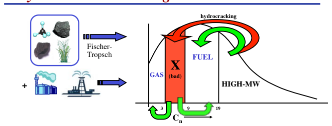


Alternative FT Route: Feedstock Flexibility and Security



Our Research: FT-Upgrade

Problem: FT gives *a full range of hydrocarbon chain lengths*



Problem: FT chemistry (and natural sources + refineries) give stochastic range of alkanes.

Medium-low MW's unsuitable for fuels (especially diesel) or use as gas (FT economics would otherwise be significantly more favorable).

Challenge: convert "mediums" ⇒ "lights" (gas) + "heavies"(diesel)
Net result: more fuel (FT diesel) = better economics

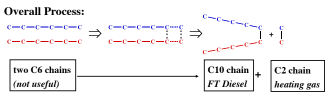
Fundamental Contribution by Our Group: FT-Upgrade via Alkane Metathesis

Two-Catalyst System

***(1) Dehydrogenation/Hydrogenation* catalysts**
(developed at Rutgers/UNC and elsewhere)

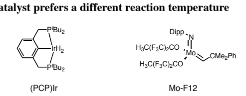
***(2) Olefin metathesis* catalysts**
(developed at MIT/Caltech and elsewhere; 2005 Nobel Prize)

Overall Process:



Goldman, Roy, Huang, Ahuja, Schinski, Brookhart, *Science*, **2006**, *312*, 257
Haibach, Kundu, Brookhart, Goldman. *Acc. Chem. Res.* manuscript accepted

Drawback for the Two-Catalyst System:
Each catalyst prefers a different reaction temperature

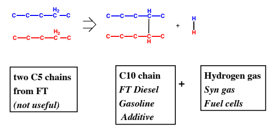


Ongoing search for new dehydrogenation and metathesis catalysts:

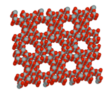
Huang, Rolfe, Carson, Brookhart, Goldman, El-Kalafy, MacArthur. *Adv. Synth. Catal.* **2010**, *352*, 125.
Yuan, Townsend, Schrock, Goldman, Muller, Takase. *Adv. Synth. Catal.* **2011**, *353*, 1985.
Haibach, Emge, Wang, Krogh-Jespersen, Goldman. *Abstracts of Papers, 244th ACS Nat'l Mtg.*

Current Research: Combining Dehydrogenation and Alkylation for Better FT Product Use

New Process for FT-Upgrade: Mild Conditions and Stable Co-Catalyst



Dehydrogenation is followed by alkylation with a Zeolite catalyst
Zeolites are microporous Al/SiO_n materials
Increasingly replacing older alkylation catalysts: HF, H_2SO_4 (kill the Ir catalyst)
Thermally stable, operate at >150°C

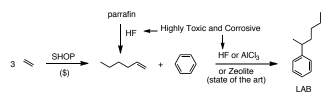


In the ZSM-5 Zeolite (L), the specific size of the pores allows for selective catalytic reactions

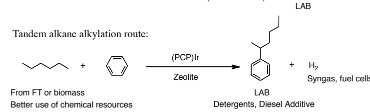
This is a feature common to all Zeolites

Other Applications of Alkane Alkylation: High-volume Chemicals from Renewable Feedstocks

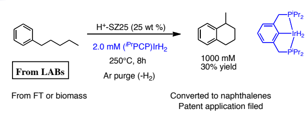
Production of linear alkylbenzenes (LABs): 10^6 TON/year
LABs: biodegradable surfactants, diesel fuel additive, other uses
Current routes are energy intensive and often hazardous:



Tandem alkane alkylation route:



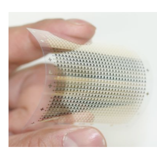
The Rutgers-Chevron Naphthalene Synthesis: Displacing Petrochemical Demand for Plastic Feedstocks



Products can be converted to polyethylene naphthalate (PEN)
PEN has superior properties to PET for a variety of advanced uses:

Inhalable anesthetic in a *gas-impermeable* PEN bottle (L), *A & A*, **104**, 1447.

Pasteurization applications for food packaging: PEN has a high enough melting point for sterilization

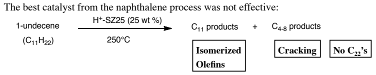


Flash memory on a PEN resin
Univ of Tokyo 2009

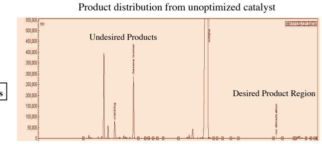
Optimization of Zeolites for the FT-Upgrade Reaction

Previous work used flow reactors and gas-phase olefins:
the reactants are forced through the Zeolite at high pressures and temperatures
Our requirement: solution phase, atmospheric pressure, T between 150°C and 250°C

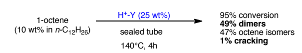
The best catalyst from the naphthalene process was not effective:



Product distribution from unoptimized catalyst

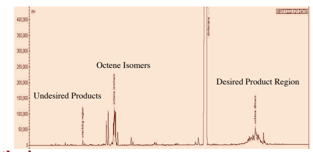


After evaluating several Zeolites (MCM-41, US-Y, ZSM-5) used previously in flow reactors:



H^+-Y is effective even at low olefin concentration (good for (PCP)Ir catalyst)
Cracking is much less prominent

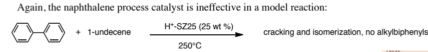
Selective dimerization of 1-octene with optimal catalyst



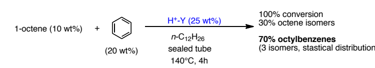
Optimization of Zeolites for the Linear Alkylbenzene Synthesis

LAB synthesis (see at left) requires an *intermolecular* reaction, which requires more energy

Again, the naphthalene process catalyst is ineffective in a model reaction:



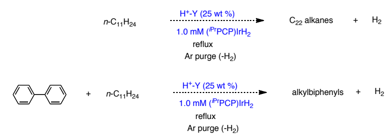
The H^+-Y Zeolite is highly effective at preventing cracking and promoting alkylation



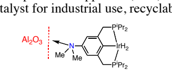
Selective alkylation of 1-octene with optimal catalyst

Current Challenge

Evaluate performance of catalysts in tandem for FT-upgrade and LAB synthesis

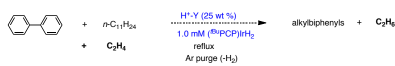


Develop a solid-supported (PCP)Ir catalyst for industrial use, recyclability



Following Huang, Brookhart, Goldman, Kundu, Ray, Scott, Vicente. *Adv. Syn. Catal.* ***2009, 351, 188.***

Develop a process using ethylene as a hydrogen acceptor



Ethylene (C_2H_4) will be widely abundant from shale gas cracking.

Efficient use!
This process uses *one* ethylene per C_{12} alkylbenzene
The traditional approach uses *12* ethylene per C_{12} alkylbenzene

Trainee Publications and Presentations from Our Group

Haibach, Kundu, Brookhart, Goldman. Alkane Metathesis by Tandem Alkane-Dehydrogenation—Olefin-Metathesis Catalysis and Related Chemistry. *Acc. Chem. Res., manuscript accepted*

Hackenberg, Kundu, Goldman. Mechanism of the oxidative addition of C-H bonds to four-coordinate (PCP)Ir(CO) complexes. *Manuscript in preparation & Abstracts of Papers, 244th ACS National Meeting*, Philadelphia.

Haibach, Emge, Wang, Krogh-Jespersen, Goldman. Basic Chemistry of POP Pincer Rhodium Complexes: Unusual Reactivity and Selectivity in Oxidative Addition and Migratory Insertion Reactions. *Manuscript in preparation & Abstracts of Papers, 244th ACS National Meeting*, Philadelphia.

Acknowledgements

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