Attrition Resistant Fischer-Tropsch Catalysts Based on FCC Supports

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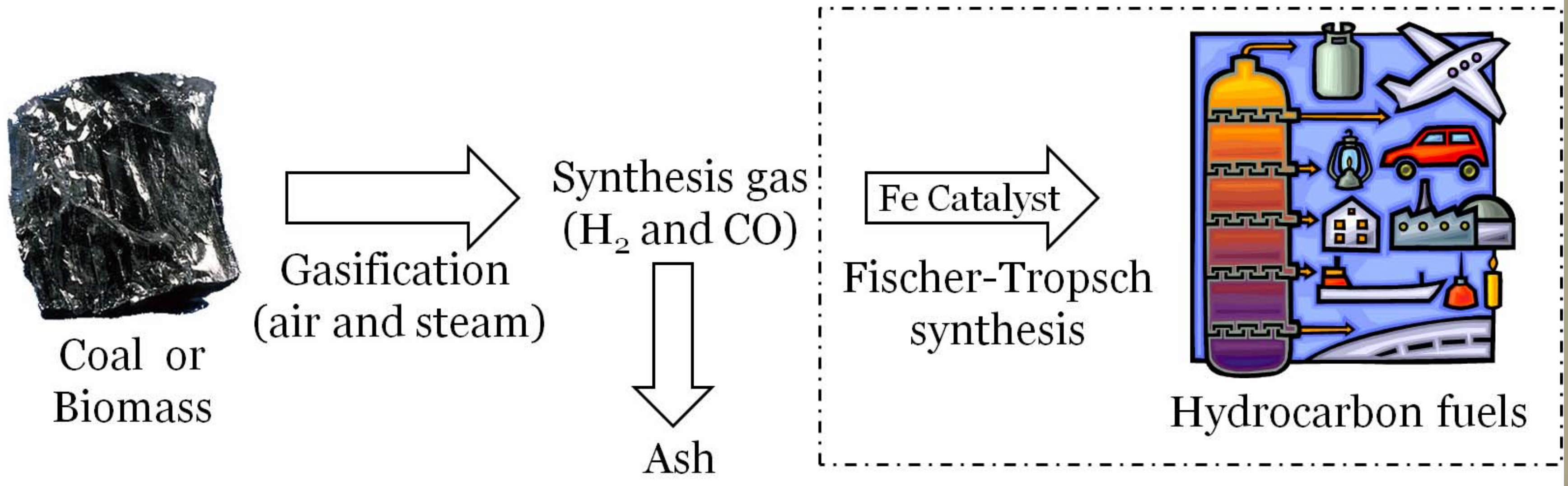
Fischer-Tropsch process

- Conversion of C_xH_y source to synthesis gas then to hydrocarbons (goal to reach high C_{10}-C_{20} selectivity)



Focus of project on Fe supported on spent FCC catalysts

Figure 1 – Conversion of coal/biomass to Fischer-Tropsch fuels

Coal Energy potential

- Four times energy equivalent in coal than oil reserves in the Middle East [IEO 2006]
- Economically competitive in the US with high crude oil prices (<$50) [Tullo 2003]

Mass of fossil fuel reserves by location	**Energy equivalent (BTUs)**
1009 billion short tons of coal in the US	2.1×10^{19}
734.4 billion barrels of oil in the Middle East	4.3×10^{18}
2565 trillion cubic feet of natural gas in the Middle East	2.6×10^{18}

Table 1 – Energy reserves in US coal compared to Middle East fossil fuels [1]

Fischer-Tropsch plants in production

- Sasol creating FT facilities in Qatar and Nigeria for production of liquid fuels

Table 2. Near-term Fischer Tropsch plants [Anon 2004]

	Plant site	
	Nigeria, Escravos	**Qatar, Ras Laffan**
Scheduled startup	2007	2005
Design capacity (Mbpd)	34	34
F-T unit technology	Sasol	Sasol
Investment estimate/daily capacity barrel ($/bbl)	23,500	23,500

Engineering issues of FT process

- Difficult to control selectivity from C_1-C_{60}+
  - Counteracted with promoters (K, Cu) and hydrocarbon cracking catalyst as the support
- Highly exothermic reaction
  - Inert liquid in SBCR can remove the heat
- Severe attrition of catalysts
  - Using spent FCC catalysts can counter this
- Cost effectiveness versus petroleum
  - Rising cost of oil in the free market reduces and improved C_{10}-C_{20} selectivity reduces this issue

Why design a SBCR FT catalyst?

- Sasol has a 10 year commercial operable SBCR for 2500 b/d (Davis 2003)
- Comparatively low reactor initial investment
- Inert fluid can quickly remove the highly exothermic FT reaction
- Permits high catalyst and reactor productivity

Why consider spent FCC catalysts as a support?

- Cost effective, attrition resistant, abundant, and comparable to fresh FCC catalysts

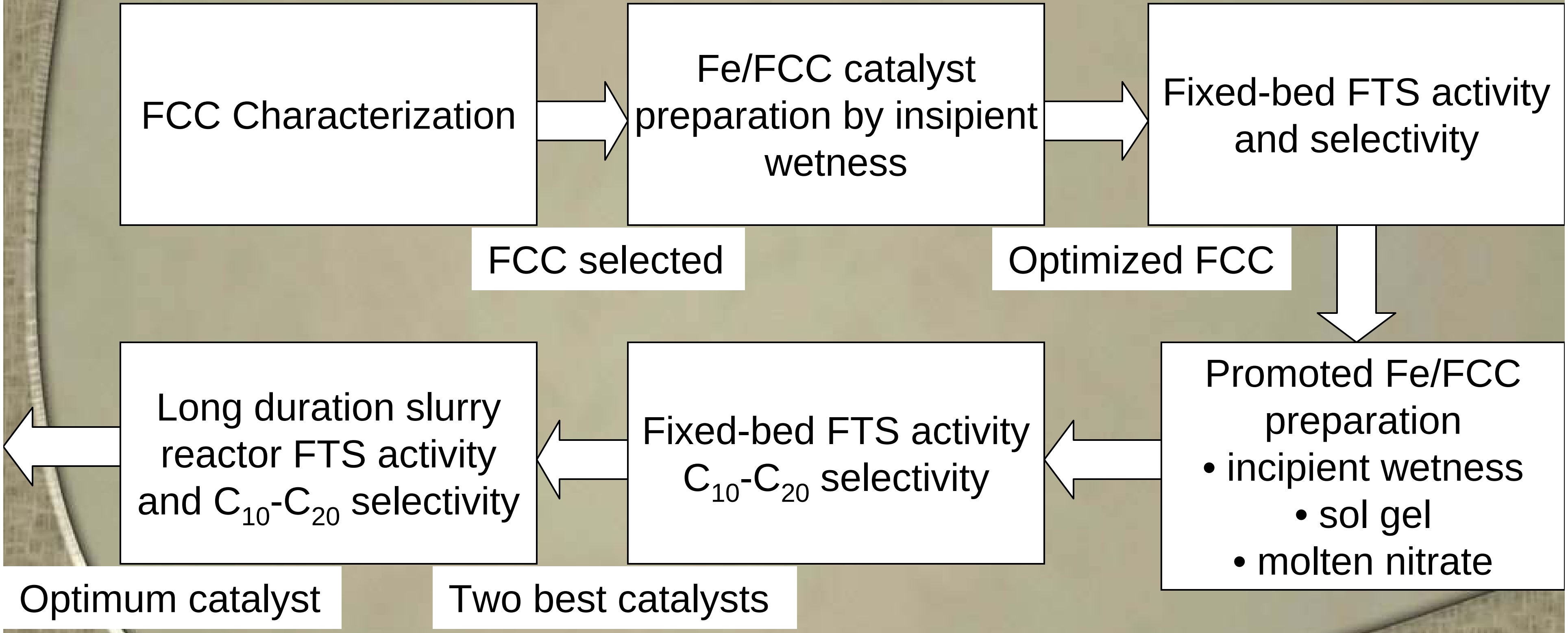
	Spent	**Fresh**
Cost ($/lb)	0.075-0.34	0.75-1.50
Size distribution (μm)	40-150	40-150
Fines (% <40μm)	Negligible	30
BET surface area	50-175	>300
5 hour attrition loss (%)	0.4	2.6
20 hour attrition loss (%)	1.2	8.0

Table 3 – Comparison between spent FCC and fresh catalysts

Why iron?

- Low H_2:CO (~0.5-0.7) ratio in biomass and coal
  - Iron exhibits the water gas shift reaction ($CO + H_2O \longleftrightarrow CO_2 + H_2$) whereas Co does not
- Cost effectiveness of Fe versus Co
- Chemical promoters can improve selectivity
  - Alkali promoters (K) suppress light end products
  - Ce, K increase activity and decrease $<C_{20}$ formation [Fiato et. al., 1998]

Proposed research plan



FCC Characterization

FCC selected

Fe/FCC catalyst preparation by insipient wetness

Optimized FCC

Fixed-bed FTS activity and selectivity

Promoted Fe/FCC preparation
- incipient wetness
- sol gel
- molten nitrate

Fixed-bed FTS activity C_{10}-C_{20} selectivity

Two best catalysts

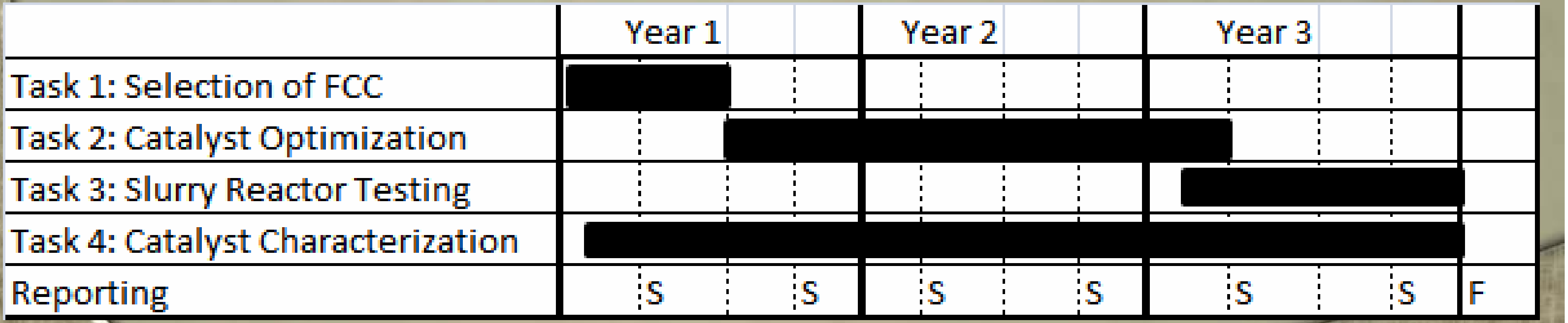
Long duration slurry reactor FTS activity and C_{10}-C_{20} selectivity

Optimum catalyst

Figure 2 – Flowchart of proposed research

Timetable for research

- Currently beginning year two of research
- No deviation from timetable
- Hampton University group working on tasks 1-4
- LSU group working on task 4



	Year 1				Year 2				Year 3				
Task 1: Selection of FCC	■	■											
Task 2: Catalyst Optimization			■	■	■	■	■	■	■				
Task 3: Slurry Reactor Testing									■	■	■	■	
Task 4: Catalyst Characterization	■	■	■	■	■	■	■	■	■	■	■	■	
Reporting		S		S		S		S		S		S	F

Table 3 – Timetable for research

Spent FCC catalysts
ICP/MS results

	FCC-1	FCC-2	FCC-3	FCC-4	FCC-5	FCC-6
Al	20.68	22.05	20.6	21.3	16.9	20.7
Ca	0.023	0.039	0.34	0.18	0.35	0.13
Fe	0.58	0.54	1.25	0.75	0.69	1.1
Ni	0.051	0.025	0.013	0.05	0.003	0.092
Pt	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Si	23.89	21.87	23.78	24.16	29.36	23.82
Ti	0.7	0.71	0.85	0.88	0.34	0.84
V	0.084	0.081	0.084	0.17	0.027	0.24
Zn	0.009	0.23	0.009	0.008	0.003	0.031
Zr	0.018	0.008	0.005	0.008	0.004	0.004
Si:Al	1.16	0.99	1.15	1.13	1.74	1.15

Table 4 – Bulk analysis of elements

BET results

- FCC-1, FCC-4 catalysts have highest BET surface areas (all within ~50%)

Sample ID	**BET surface area (m^2/g)**
FCC-1	158.1
FCC-2	101.7
FCC-3	112.3
FCC-4	153.0
FCC-5	136.9
FCC-6	106.4

Table 5 – BET surface area of spent FCC catalysts

Reaction results

- CO conversion and product distribution are encouraging as a proof of concept
- Reaction performed at mild Fischer-Tropsch conditions (to prevent liquid products)

15 % Fe supported on spent FCC catalyst (unpromoted)	
% CO conversion	23.6
Hydrocarbon product distribution, wt. percentages	
C_1	20.6
C_2-C_4	53.2
C_5+	26.2

Table 6 - Fixed bed reactor results, T=250^{o}C, 1MPa, H_2/CO=1, WHSV=0.77hr^{-1}

Conclusions

- Little difference in commercial spent FCC catalysts in bulk composition and BET (surfaces may be different, future work will resolve this)
- Unpromoted Fe-supported on FCC shows moderate FT activity

Future work

- Further characterization (CO_2 TPD, H_2 TPR, CO TPD) and reaction testing on both spent FCC materials and Fe on FCC will be interesting
- If attrition testing gives favorable results Fe on spent FCC catalyst this may develop a future catalyst in SBCR FTS reactors

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