Hetero-Polyaromatic Ring-Opening Reactions in $scCO_2$

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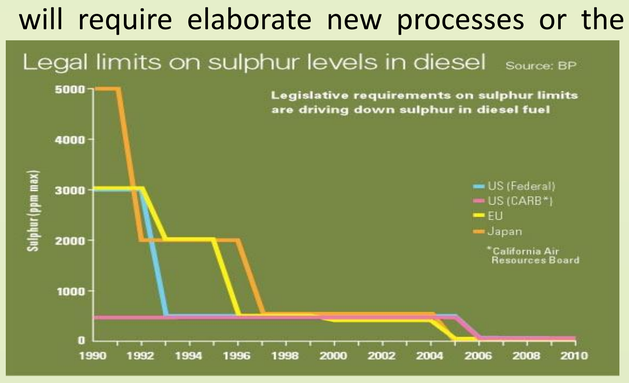
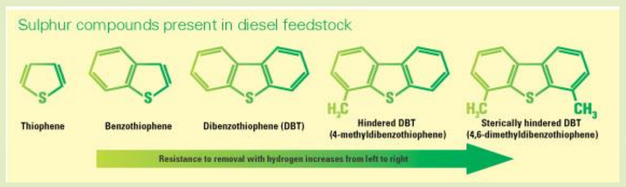
The Challenge

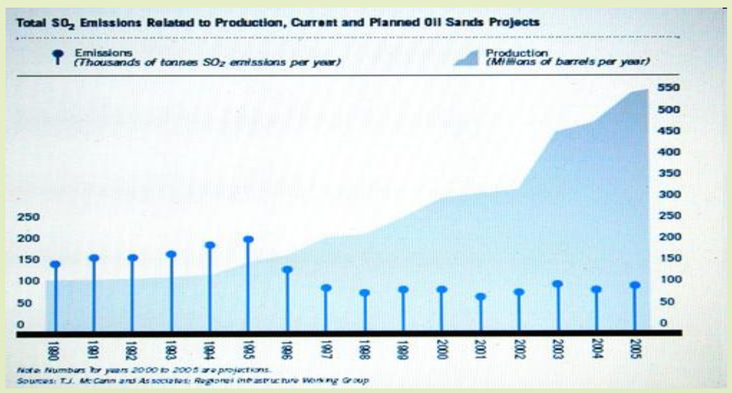
• Production of cleaner fuels from increasingly low-grade feedstocks and non-edible biomass sources.

• In the EU, planned reduction of sulfur levels in gasoline and diesel to 10 wt ppm for 2009 will require elaborate new processes or the





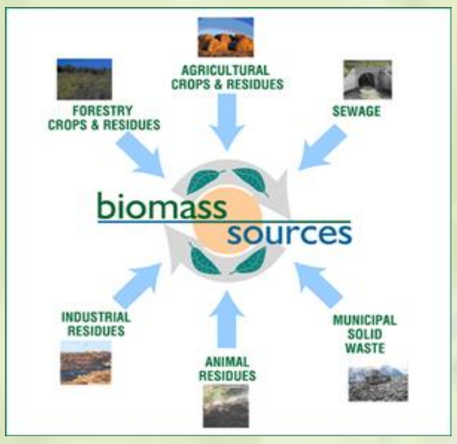
• The essential component of ultra-deep HDS is the development of highly active hydrogenating catalysts in a medium that supports this activity. To achieve energy sustainability that satisfies current and impending environmental regulations of sulfur and nitrogen levels in transportation fuel, a clean conversion technology and methodology is fundamental.



• In January 2007 the European Union agreed on a target to make biofuels 10% of fuels consumed in the transport sector by 2020.[2]

• Biomass fuels are derived from industrial processing, such as forestry and wood products, agriculture residues and wastes, municipal solid wastes and fast growing energy crops.

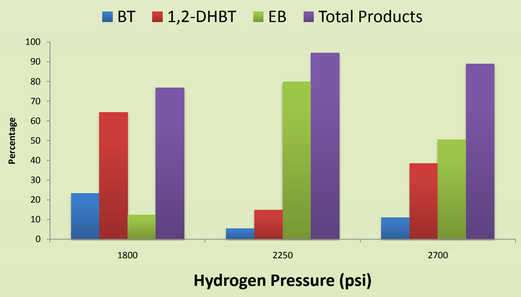
• Biomass electrical generation or biopower is second only to hydropower as a renewable energy source.[3]



➢ **The main objective of this project is to explore the utility of $scCO_2$ for upgrading and hydrotreatment of oil sand ,coal , biomass and transportation fuels using less energy than conventional processes.**

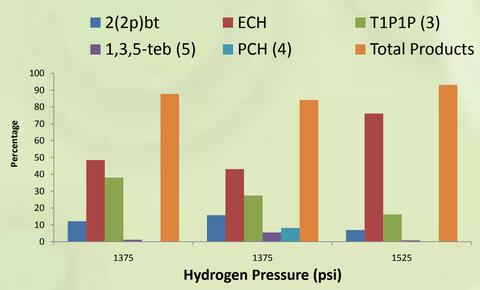
➢ **$ScCO_2$ has the potential to play several crucial roles in bitumen upgrading and the advancement of integrated clean coal and biomass technologies.**

Results



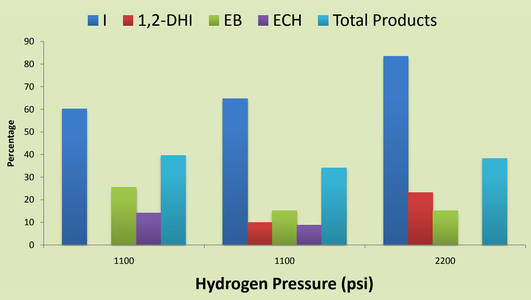
Model Compounds for HDS/HDN in $scCO_2$

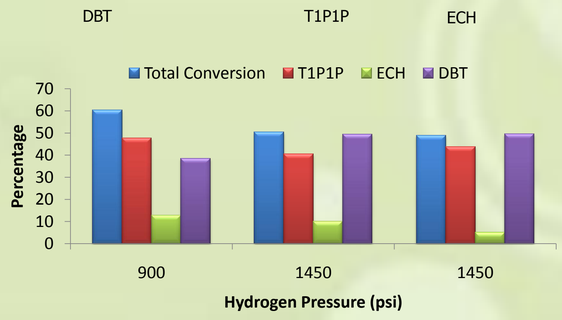
Benzothiophene HDS and indole HDN reactions were performed in $scCO_2$ using various heterogeneous catalyst. For benzothiophene, HDS products were predominant using Pd/Al_2O_3, whereas the hydrogenation pathway was observed when using Rh/Al_2O_3. Reactions were performed over the temperature range of 100-225 ^oC, with the optimal HDN temperature being 200 ^oC. The fully hydrogenated HDN product (**ECH**) was observed in $scCO_2$ only with the commercial catalysts; however no such product was observed when using hexane as the reaction medium.



Combined HDS/HDN in $scCO_2$

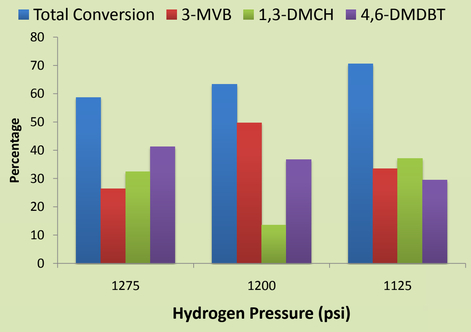
Combined HDS/HDN experiments on 2(2-pyridyl)benzothiophene and $(NH_4)_2S_2O_3$ as the sulfiding agent were performed using far lower temperatures than conventional processes.[4] These reactions showed high levels of hydro-cracking products, with the major one being ethylcyclohexane. Up to 76% ethylcyclohexane was observed; an unprecedentedly high yield. In this case, the synthesized catalyst $[CoMoS_4/TiO_2\text{-}Al_2O_3]$ performed as well as the commercial catalyst.



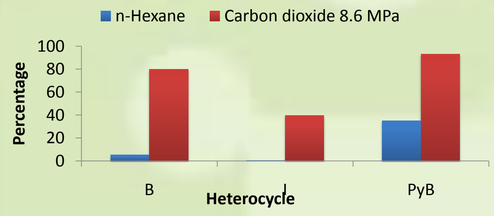


➢ Hydrotreating processes must have the capacity to desulfurize highly refractory alkyl-dibenzothiophenes (alkyl-DBTs) while performing the complete hydrogenation of aromatic molecules.[5]

4,6-DMDBT 3-MVB 1,3-DMCH



Hydrogenolysis Results for HPHs in n-Hexane and $scCO_2$



Future Work

Synthesized transition metal catalysis under investigation

$CoMoS_4/TiO_2\text{-}Al_2O_3$
➢ Superior in HDS/HDN experiments

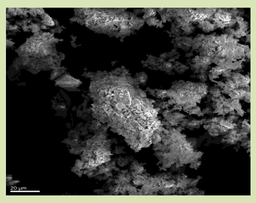
$NiW/TiO_2\text{-}Al_2O_3$
➢ For high sulfur diesel HDS experiments

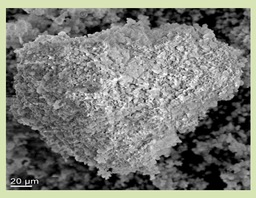
$CoMoS_4/Al_2O_3$
➢ For bitumen upgrading

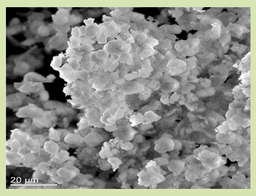
$NiMoW/Al_2O_3$

NiMo/MCM-48

NiMo/Al-MCM-48







Conclusions

➢ Superior HDS/HDN conversions are obtained in $scCO_2$ in comparison to conventional solvents.

➢ Ring-opening and HDS/HDN observed under remarkably mild conditions (100-200^oC lower than comparative conventional processes).[4]

➢ Encouraging ground work paves the way for production of ultra-clean fuels.

References

1) Off. J. Eur, Commun. L76 (**2003**) 10
2) www.energysavers.gov
3) http://ec.europa.eu/environment
4) R.G. Leliveld, S.E. Ejisbouts, Catal. Today 130 (**2008**)183
5) Baldovino-Medrano, V.G., Giraldo, S.A., Centeno, A.; J Mol Cat (**2009)** 127-133