

The relevance of catalytic pyrolysis for the production of bio-fuels
Nandan Cleantech and NCCR
21st April 2013

The production of bio-fuels has assumed significant importance due to economic and environmental considerations[1]. There are various process steps involved in this technology. One of the process steps that has received considerable attention is the fast (why and the need for fast?) pyrolysis that can yield high liquid yields with specific composition, but must be capable retaining majority of the energy content of the bio-fuel. These limitations are required simply to make bio-fuel to be compatible to the petroleum based fuels that are being extensively employed in the present days. The essential consideration in devising proper pyrolysis step is to remove selectively the oxygen component found in the bio-fuel. This oxygen removal can be achieved either by hydrogenation (conventionally known as hydro-treating) or by splitting the molecule (termed as cracking). Both these process steps are well known and practiced in oil industry today. Catalytic cracking for the production of biofuel is achieved by de-oxygenation through simultaneous dehydration, decarboxylation and decarbonylation reactions and these reactions have been shown to proceed in the presence of ordered microporous zeolites catalysts. Though the catalytic pyrolysis has been known, the search for appropriate catalyst system is still on since, it is necessary that one not only obtains the desired levels of conversion (which should be of the order of 90% or above), the hydrocarbon content should be optimum. This means the organic functional like carbonyls, acids, esters phenols and ethers must be suitably handled so as to optimize the hydrocarbon content which provide the necessary fuel value. The literature is abundant[2-3] on these attempts especially with respect to finding appropriate catalyst system and also identifying suitable process formulation. There have been attempts to couple pyrolysis and catalytic cracking in a single flow without the intermediate separation of the cracked products from the points of view of economics of the process and also to avoid the possible catalytic deactivation by in situ coke formation or other condensed products. A variety of in situ techniques [4] (like IR, XPS, TPD) have been adopted to identify the removal oxygenates especially carboxylic and ester functionalities since the presence of these functionalities will affect the hydrocarbon yield and thus reduce the fuel value. The type of studies that have been reported in literature are: (i) Evaluating various catalyst systems that will preferentially and selectively produce hydrocarbons that can be used as fuels or fuel blends. Though this can be achieved both by hydrotreating and cracking the later is examined to a greater extent due to reasons like technology is well known and also process simplicity. In these studies the optimization has been focused on temperature, pressure, and adopting suitable analytical technique for unambiguous identification of the components of the product stream. Another major factor is to examine the exact ratio of catalyst to the biofuel content in a semi-continuous or continuous mode. In the following few lines, the recent research activity in this area is briefly summarized.

(i) Various types of catalysts systems have been evaluated for their performance and also to find guidelines for catalyst design. Not only conventional FCC (Fluid Cracking Catalysts) systems but also various types of modifications have also been evaluated. In addition, the recent meso-porous systems like MCM type with various types of substitutions have been evaluated with a

view to optimize the hydrocarbon yield. [5-10]

(ii) Various process variables mostly on laboratory scale reactors like super critical water method to increase heating value, effect of hydro-treatment to increase oxygen removal [11]

(iii) Another critical parameter that has been studied is the catalyst to bio-mass ratio [12]

(iv) Hydrotreating versus catalytic cracking [13]

(v) Reactor design and configuration

The following aspects have not been paid much attention

(i) Characterization of the fuel parameters produced by catalytic pyrolysis and thus optimising the pyrolysis parameters. Only higher or lower yield is reported but the comparison with respect to petroleum based fuel has to be stipulated.

(ii) The reactor design in detail is not yet available completely. [14]

(iii) The pretreatment procedures required for various catalyst system is not yet established. [15]

(iv) The selection of the appropriate catalyst has not yet been established though results on a number of catalyst systems are available.

(v) The predictive capacity of bio-oil quality on the basis of input parameters is not yet shown. [16-17]

This summary note on the status of catalytic pyrolysis route shows that there are various gaps in our knowledge in transforming this technology into a viable technology. The teams are considering this possibility of transforming this laboratory based technology to a manufacturing matured technology.

0.1 References

1. Richard French and Stefan Czernik, Catalytic pyrolysis of biomass for biofuels production, *Fuel processing Technology*, 91, 25-32 (2010).
2. Le Zhang, Ronghou Liu, Renzhan Yin and Yuanfei Mei, Upgrading bio-oil from biomass fast pyrolysis in china A review, *Renewable and Sustainable Energy Reviews*, 24,66-72 (2013).
3. A.V Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Bio-mass and Bio-energy*,38, 68-94 (2012).
4. Chang Bo Lu, Jian Zhong Yao, Wei Gang Lin, and Wen Li Song, Study of biomass catalytic pyrolysis for production of bio-gasoline by on line FTIR, *Chinese chemical letters*, 18, 445 (2007)
5. T.S.Nguyen, M.Zabeti, L.Lefferts, G.Brem and K.Seshan, Catalytic upgrading of biomass pyrolysis vapours using faujasite zeolite catalysts, *Biomass and Bioenergy* 48, 100-110 (2013).
6. Kostas S.Triantafylidis, Eleni F.Iliopoulou, Eleni V.Antonakou, Angelos A.Lappas, Hui Wang and Thomas J.Pinnavaia, *Microporous and mesoporous Materials*, 99, 132-139 (2007).
7. A.Aho, N.Kumar, A.V.Lashkul K.Eranen, M.Ziolek, P.Decyk, T.Salmi, B.Holmbom, M.Hupa and D.Yu Murzin, Catalytic upgrading of woody biomass derived pyrolysis vapours over iron modified zeolites in a dual fluidized bed reactor, *Fuel*, 89, 1992-2000 (2010).
8. Ofei D Mante, F.A.Agbilevor and R.McClung, A study of catalytic pyrolysis of biomass with Y zeolite based FCC catalyst using response surface Methodology, *Fuel*, 108, 451-464 (2013).

9. S.D.Stefanidis, K.G.Kalogiannis, E.F.Iliopoulou, A.A.Lappas and P.A.Pilavachi, In Situ upgrading of biomass pyrolysis vapours Catalysts screening on a fixed bed reactor, *Biosource Technology*, 102, 8261-8267 (2011).
10. David J.Mihalcik, Charles A Mullen, Akwasi A.Boateng, Screening acidic zeolites for fast pyrolysis of bio-mass and its components, *Journal of Analytic and Applied Pyrolysis*, 92, 224–232(2011).
11. Wan Nor Roslam Wan Isahak, Mohamed W.M.Hisham, Mohd Ambar Yarmo and Taufliq-yap Yun Hin, A review of io-oil production from biomass by using pyrolysis method , *Renewable and sustainable energy reviews*, 16,5910-5923 (2012).
12. S.Thangalazhy-Gopakumar,Sushil Adhikari, Ram B Gupta, Maobing Tu, and Steven Taylor, Production of hydrocarbon fuels from biomass using catalytic pyrolysis under helium and hydrogen environments, *Biosource Technology*, 102, 6742-6749 (2011).
13. Yuxin Wang, Tao He, Kaituo Liu, Jinhu Wu, Yunming Fang, From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing Hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis, *Biosource Technology*, 108, 280-284 (2012).
14. Guray Yildiz, Marty Pronk, Marko Djokic, Kevin M Van Green, Frederik Ronsse, Ruben Van Duren and Wolter Prins, Validation of a new setup for continuous fast pyrolysis of biomass coupled with vapour phase upgrading, *Journal of Analytic and Applied Pyrolysis*, (2013).
15. Judit Adam, Eleni Antonakou, Angelos Lappas, Michael Stocker, Merete H Nilsen, Aud Bouzga, Johan E.Hustad and Gisle Oye, Insitu catalytic upgrading of bio-mass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials, *Microporous and mesoporous Materials*, 96, 93-101 (2006).
16. W.N.R.W.Isahak et al., *Renewable and sustainable energy reviews*, 16,5910-5923 (2012).
17. M.C.Samolada et al, Production of bio-gasoline upgrading, *Fuel*, 77, 1674 (1998).