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CONVERSION OF BIOMASS TO FUELS AND CHEMICALS VIA THERMOCHEMICAL PROCESSES

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Abstract
Biomass fast pyrolysis is a very promising thermo-chemical process for the production of liquid fuels (bio-oil) and chemicals. However, some properties of the bio-oil serve as primary obstacles for its further application and commercial scale-up. Upgrading of bio-oil can be achieved either during or downstream of its production process. The first case refers to the application of heterogeneous catalysis during pyrolysis (catalytic biomass pyrolysis). This technology for fuels production will be extensively reviewed in this seminar from both process and catalysis side. CPERI pilot plant and bench scale experimental results using different types of catalysts will also be discussed in details. From the work till today it seems that biomass catalytic pyrolysis decreases the bio-oil yield but significantly improves its composition by achieving high deoxygenation rates. Bio-oil upgrading techniques after its production will also be discussed in this seminar. Three upgrading options will be covered: a catalytic hydrodeoxygenation under high pressure in the presence of hydrogen, a catalytic cracking utilizing zeolitic catalysts and a co-processing with refinery streams.

Introduction
In this lecture we will focus on biomass thermal and on biomass catalytic fast pyrolysis towards fuels and chemicals production. We will review the literature on catalytic pyrolysis and we will focus on some latest results from CPERI work on these processes. The upgrading of bio-oil towards fuels productions through hydrodeoxygenation, catalytic cracking and co-processing will also be discussed.

Results and discussion

The biomass fast pyrolysis process is a major thermo-chemical process for converting solid biomass to fuels and chemicals. Pyrolysis offers high yields of liquid product (bio-oil), however, this liquid has many drawbacks (corrosiveness, instability under storage and heating conditions, immiscibility with petroleum fuels, high acidity, high viscosity and low calorific value) that limits its commercial usage. For this reason the technology of biomass catalytic pyrolysis has extensively studied the last year. In this technology a heterogeneous catalyst is used as a heat carrier in the pyrolysis reactor for the in-situ upgrading of the quality of the bio-oil by minimizing its undesirable properties. The key process technology for biomass catalytic pyrolysis is based on circulating fluid bed reactor which permits continuous catalyst regeneration. This technology will be discussed in details in this seminal along with the catalysts type used in the literature for this process.

In the seminar emphasis will be given on CPERI results on catalytic pyrolysis using various types of microporous and mesoporous catalysts. The catalysts effects on product yields and bio-oil quality will be discussed [1,2]. From the work till today it seems that the type of catalyst has a significant effect on the pyrolysis products. The use of catalytic materials does not favor the production of the liquid (bio-oil). The more active the catalyst (higher surface area), the less liquid is produced. Zeolite catalysts cause secondary reactions to the primary pyrolysis products leading to lighter products and coke. These secondary reactions crack the bio-oil vapor compounds to lighter ones producing gases, coke and water. On the other side the presence of catalyst causes a significant change to the bio-oil's composition. By increasing the catalyst surface area, the hydrocarbons concentration increases. With the most active catalyst this concentration is almost double compared to that from the non-active material. Carbonylic compounds were also decreased. However, the most important effect of catalysts is on the heavy compounds, which are drastically decreased. Results from the evaluation of about 15 catalysts will be presented in this seminar and will show that by the appropriate catalyst selection a highly deoxygenated bio-oil can be produced.
The further upgrading of the thermal or catalytic bio-oil will also be covered in this seminar. Three types of upgrading processes will be examined: the hydrodeoxygenation, the catalytic cracking and the co-processing with refinery feeds. Results from literature for all these upgrading steps will be presented regarding optimization of operating conditions, reactors and catalysts. The CPERI technology on this issue that is based on a thermal hydrotreating step following by distillation and catalytic cracking of the heavy fractions will also be presented.

Conclusions

The conversion of biomass to fuels and chemicals from pyrolysis process is technically feasible and today this technology is on a demonstration phase. Pyrolysis is an old technology producing a fuel (bio-oil) that has many drawbacks, however, the use of heterogeneous catalysis (biomass catalytic pyrolysis) can assist in the production of a better quality bio-oil. Catalytic biomass pyrolysis has recently gained a lot of attention in literature focusing on new tailored catalysts and process conditions. CPERI has developed technology on this process using circulating fluid bed reactor. The main conclusion from the research work till today is that the catalysts affect the primary heavy pyrolysis products by cracking them towards coke and gases. Thus, we can achieve lower yields of bio-oil but with a better quality, since it contains less heavy oxygenates and a higher degree of deoxygenation.

References

1. A.A. Lappas, V.S. Dimitropoulos, E.V. Antonakou, S. S. Voutetakis, and I. A. Vasalos, *Ind. Eng. Chem. Res.* **2008**, 47, *742-747.*
2. A.A. Lappas, E.F. Iliopoulou and K. Kalogiannis, **2010**, ed. (RSC Publishing), *263-287.*