CHARACTERIZATION AND UPGRADING OF A BIO-OIL PRODUCED BY PYROLYSIS OF BIOMASS

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ABSTRACT

This paper presents the results obtained in the characterization of a pyrolytic oil with a high nitrogen content. The oil was separated in fractions by liquid chromatography. The first two fractions contain hydrocarbons and monophenols respectively. Most of the relevant compounds have been identified in both fractions. Nitrogen is mainly contained in the compounds constituting the last fraction. The upgrading was done by treatment under high pressure of hydrogen with sulfided supported nickel-molybdenum and cobalt-molybdenum. Both catalysts were active in the transformation but NiMo gave higher yields in HDN and HDO. The upgrading was facilitated by the presence of hydrogen donor compounds such as pure tetralin on a fraction of the hydrotreated oil.

INTRODUCTION

A number of processes allow us to convert biomass into liquid fuels or chemicals. These processes have been reviewed recently and it can be seen that a very wide range of liquid products can be produced (1). The processes can be classified into two groups: 1) high pressure processes and 2) low pressure pyrolytic processes. In the first group, the transformation of the biomass is accomplished under high pressure of hydrogen, carbon monoxide, water and nitrogen solely or combined and with or without catalysts. As early as 1924, Bowen and Nash (2) reported that more than 80% of cotton cellulose was converted into liquids and gases in the presence of nickel and alumina catalysts under high pressure of hydrogen. In the '70s the Pittsburgh Energy Research Center of the Bureau
of Mines in the USA (3) developed a process in which the biomass is reacted in the presence of an alkali catalyst ($\text{Na}_2\text{CO}_3$) with carbon monoxide and water but this process had a limited success because the product could only compare with N°2 and N°6 fuel oils. At present, and based on this concept, the University of Arizona (4) is conducting research on direct liquefaction using very concentrated biomass slurries (60% of wood in biomass oil). Recently Meier et al. (5) accomplished the direct liquefaction in a slurry oil process using a commercial palladium on an active charcoal catalyst and thus obtaining one of the best oils (in terms of physical and chemical properties) ever produced, with a yield of close to 40%.

Regarding the low pressure pyrolytic process, char, oil and gases are obtained. In recent years, the concept of fast pyrolysis has been developed and by the careful control of both temperature and heat transfer the yield to bio-oil can be raised to 60-70% but to the best of our knowledge this yield has been obtained only at the small pilot plant level, as shown in the works of the University of Waterloo (6,7) and Georgia Tech. (8). A very interesting process using the vacuum pyrolysis concept is currently being developed by Roy et al. (9), where the bio-oil yield is close to 50%.

The bio-oils produced using these methods are usually used in direct combustion even though they rarely meet the standards required for fuels. They are very viscous, corrosive, not completely volatile, present high oxygen contents and mix badly with conventional fuels. To be able to use bio-oils as fuels, they must be processed to reduce viscosity, corrosivity, heteroatom contents and improve volatility. One method proposes a deoxygenation without reducing gases through a simultaneous decarboxylation and dehydratation over zeolitic catalysts. This system can transform only the volatile fraction of the bio-oils. Another method proposes the upgrading of the bio-oils by a treatment under high pressure of hydrogen using noble metals (10) as catalysts and sulfided cobalt-molybdenum and nickel-molybdenum (11,12,13). In this manner oxygen, nitrogen and sulfur are eliminated as water, ammonia and hydrogen sulfide respectively. Hydrocracking and hydrogenation of large non-volatile molecules also occur.

The results presented here deal with the hydrotreatment of an oil produced by pyrolysis from wastes of the olive oil industry at a demonstration unit located in Raiano (Italy). The reactor is a fluidized bed. The biomass feed rate can vary between 350 and 500 kg/h and typical operating temperatures are between 450 and 550°C. The high nitrogen