CO-LIQUEFACTION OF CELLULOSIC BIOMASS AND POLYPROPYLENE TO PRODUCE LIQUID FUEL

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The development of efficient technologies for the conversion of cellulosic biomass to liquid fuels is an important research area. At present, liquefaction plants are investigating the use of small-scale, simple processes that convert a combination of cellulosic biomass and waste plastics into high quality light oil at low pressures and temperatures, using a solvent-based approach. This paper describes the co-liquefaction of cellulosic biomass (ground Japanese cedar) with waste plastic (polypropylene) at 400 °C and summarizes the effects of the added plastic on the yield and quality of the resulting oil. The data obtained through this work demonstrate that co-liquefaction results in a higher conversion of the starting materials than is the case for either pure cellulosic biomass or polypropylene.

Keywords: wood biomass, waste plastic, co-liquefaction, liquid fuel, solvent circulation process

INTRODUCTION

The development of alternatives to fossil fuels is currently of significant practical importance because fossil-based resources, such as petroleum, may well be exhausted in the near future. In addition, the international community has a responsibility to reduce emissions of carbon dioxide, the greenhouse gas associated with the conversion of fossil resources to energy. Wood-based biomass is an alternative to fossil fuels that has attracted attention because it is renewable by photosynthesis in a relatively short time frame and its use as an energy source is carbon neutral.[1]

The handling and transport of cellulosic biomass is, however, labor intensive and so the collection and distribution of this material can be costly. For this reason, it is preferable to convert cellulosic biomass to an alternative fuel, such as diesel oil or heavy oil, at locations near the sawmills where the biomass is generated, and a direct liquefaction process incorporating a circulating solvent system has been investigated for this purpose.[2] This liquefaction process has a number of benefits, including high efficiency, because constant replenishing of the catalyst and solvent is not required. In addition, the heavy fraction of the liquefaction oil produced in the system is itself employed as the circulating solvent, which allows the use of mild reaction conditions, including low pressures. Unfortunately, studies concerning this process have also identified that the biomass liquefaction oil used as the process solvent absorbs and conveys significant heat as it circulates, and this heat can lead to over-decomposition of the biomass, as well as undesirable condensation reactions between the liquefaction products. As a result of these problems, it can be difficult to predict the quantity of solvent required to operate such a system.[3] A potential means of addressing this issue is to use mineral oil as solvent within the liquefaction process instead, because it is a mixture of saturated hydrocarbons and is essentially inert. Another possible approach, which has been considered for the provision of a steady, stable circulating solvent within the process, is the co-liquefaction of waste plastic with the cellulosic biomass. In the work presented herein, the co-liquefaction of wood-based biomass (ground Japanese cedar) with the common plastic polypropylene (PP) was investigated with regard to product yields and other factors.

EXPERIMENTAL
Materials
Japanese cedar wood was ground in air using a tower mill to produce particles with a median diameter of 112 μm. The resulting ground material was dried at 110 °C for 90 minutes under vacuum prior to use. Mineral oil (Cosmo Puresafty 100, Cosmo Oil Lubricants Co.) and a liquefaction product we term "solvent fraction" (as defined below) were both used as solvents in liquefaction trials. PP was sourced from Sigma-Aldrich Co.

Co-liquefaction trials
A total combined mass of 30 g of ground Japanese cedar and PP, together with a combined mass of 90 g of mineral oil, were charged into a 300 ml autoclave equipped with an electromagnetic induction-type stirrer. The solvent fraction was used in the circulation trials instead of mineral oil. The mass ratio between Japanese cedar and PP within the 30 g charge was 8:2. After the autoclave was sealed, the air inside was replaced with nitrogen gas at a pressure of 0.5 MPa and the autoclave was heated to 400 °C by an external electric furnace with stirring at 200 rpm. After allowing an appropriate time interval for the liquefaction reaction, the autoclave was air-cooled and the internal headspace gases were collected. The chemical composition of this product gas mixture was determined by gas chromatography with thermal conductivity detection (GC-TCD). The liquid slurry from the autoclave was also collected and separated into fractions on the basis of boiling point using simple distillation. The fractions collected were those with initial boiling point to 220 °C (gasoline fraction), 220 to 350 °C (light oil fraction) and 350 °C or more (tank bottom fraction). The tank bottom fraction was subsequently further separated into two fractions: toluene-insoluble (which we termed "residue") and toluene-soluble (the "solvent fraction"). The solvent fraction was further separated, using both alumina column chromatography, into a benzene fraction (the non-polar material) and a benzene-methanol fraction (polar). The water content of the gasoline fraction was analyzed by Karl Fischer titration. In addition, both the gasoline and light oil fractions were analyzed via gas chromatography-mass spectroscopy (GC-MS) using a polar capillary column. Finally, structural analyses of the residue, non-polar and polar fractions were carried out using Fourier transform infrared spectroscopy (FT-IR).

Hydrogen abstraction trials
In order to assess the capacity of the liquefaction products for hydrogen abstraction, a combination of ground Japanese cedar and tetralin was also subjected to co-liquefaction in the same manner as described above. The resulting slurry was collected and separated into hexane-insoluble and hexane-soluble fractions. The hexane-soluble fraction was subsequently analyzed by GC-MS.

Diesel oil miscibility trials
The light oil fraction of co-liquefaction of 20 wt% was mixed with diesel oil of petroleum origin of 80 wt%. After it had been shaken 30 times, it was left for 42 hours. Afterwards, the liquefaction oil phase and the diesel oil phase were weighed.

RESULTS AND DISCUSSION
Assessment of interactions
The product yields obtained following the liquefaction and co-liquefaction of Japanese cedar and PP are shown in Fig. 1 and the FT-IR spectra of the resulting residues are presented in Fig. 2.
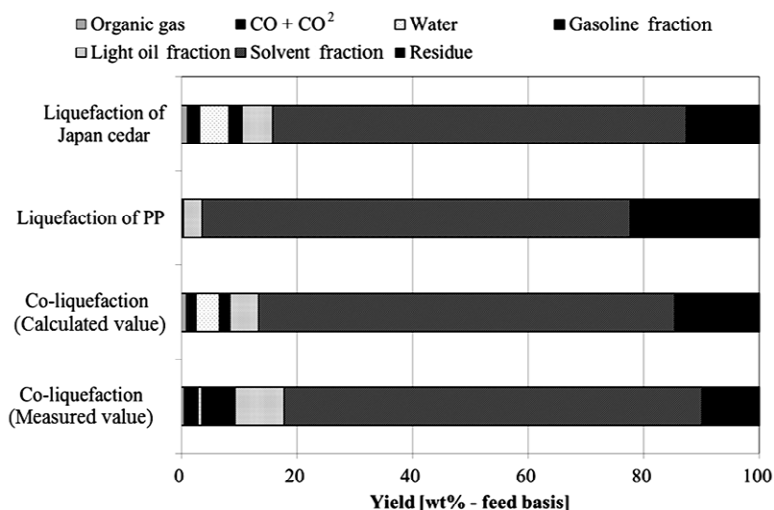

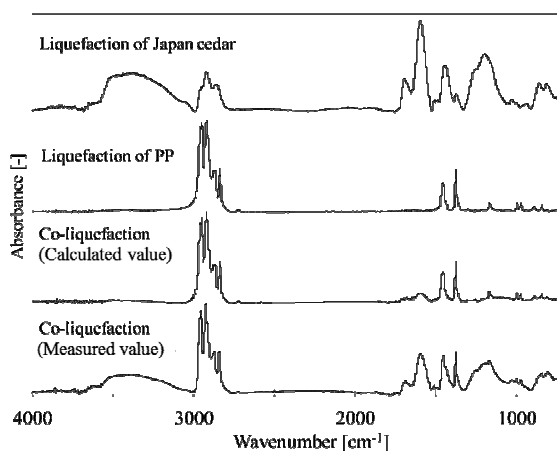Figure 1: Product yields following liquefaction and co-liquefaction of Japanese cedar and polypropylene

Figure 2: FT-IR spectra of residue materials resulting from liquefaction and co-liquefaction of Japanese cedar and polypropylene

Figure 3: GC-MS chromatogram of hexane-soluble fraction obtained from Japanese cedar and tetralin

For the purpose of comparison, a calculated product yield summary and calculated IR spectrum for the co-liquefaction are also included. The calculated yields and spectrum were produced by taking the arithmetic average of the results for the individual pure cedar and PP liquefactions and thus can be considered the theoretical or expected co-liquefaction yields and spectrum.

From Fig. 1, it can be seen that the actual measured co-liquefaction yields of both water and residue were lower than the calculated average values and that the measured gasoline and light oil fraction yields were higher than the corresponding calculated values. In addition, the measured co-liquefaction residue yield appears closer to the residue yield resulting from the liquefaction of pure Japanese cedar than to the theoretical calculated value.

From Fig. 2, it can be noted that there is a peak of the hydroxyl group in the vicinity of 3400 cm⁻¹ in the IR spectrum of the actual measured co-liquefaction residue and it looks like the spectrum of the residue of the Japanese cedar. However, there is little peak of the hydroxyl group in the calculated average spectrum.

From the above results, we can arrive at some conclusions regarding the nature of the interaction between Japanese cedar and PP during the co-liquefaction process. It has been reported that Japanese cedar liquefaction products undergo mutual dehydration or condensation reactions and that these products are responsible for the residue resulting from the liquefaction process.[3] Because we observed decreased yields of both water and residue during the co-liquefaction, we suggest that the Japanese cedar and PP liquefaction products
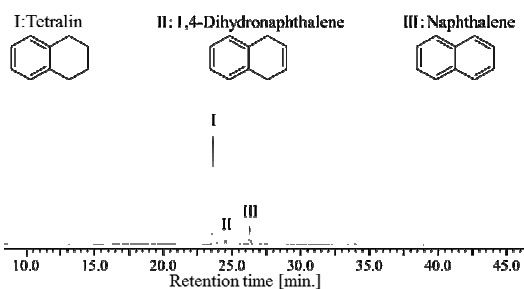
underwent condensation, so that the yield of cedar condensation products was reduced. The results also suggest that the cedar liquefaction products promote the decomposition of the PP, because the yields of the light oil and gasoline fractions increased in the case of co-liquefaction, while the IR spectrum of the co-liquefaction residue was nearer that of the pure cedar than the calculated average value.

Hydrogen abstraction

The GC-MS chromatogram obtained for the hexane-soluble fraction of the product mixture resulting from the hydrogen abstraction trial is shown in Fig. 3. This chromatogram exhibits peaks for both naphthalene and 1,4-dihydronaphthalene, demonstrating that a portion of the tetralin solvent has undergone hydrogen abstraction and confirming that there are hydrogen acceptors among the Japanese cedar liquefaction products. We propose that the same hydrogen acceptor species are responsible for promoting the decomposition of PP, as observed in the earlier trials.

Solvent circulation

The product yields for the co-liquefaction circulation trials are shown in Fig. 4, and Fig. 5 presents the FT-IR spectra of residues resulting from these experiments. The solvent compositions and polar compound FT-IR spectra are given in Fig. 6 and Fig. 7.

The plots in Fig. 4 show that the residue and solvent fraction yields exhibit very little change following repeated circulation of the material, whereas the yields of the gasoline and light oil fractions have increased by the second circulation,

but do not change after the third. The yield of the solvent fraction increases from the first to the second circulation, but then remains relatively constant. The spectra in Fig. 5, meanwhile, demonstrate that the composition of the residue exhibits only minimal change on circulation. The data in Fig. 6 show that the proportion of polar compounds in the solvent increases up to the third circulation, but remains constant afterwards, and the spectra in Fig. 7 show that the hydroxyl peak at 3000 cm^{-1} increases between the first and second circulations and then remains constant.

From these data, it appears that the polar compounds in the solvent, whose proportions increase with circulation, are not associated with the generation of the residue, because the residue yield does not increase simultaneously. This

conclusion is also supported by the residue IR spectra, which do not show any appreciable increase with circulation in the region of the spectra associated with the hydroxyl groups of the polar compounds. These results also show increasing generation of the gasoline and light oil fractions from the solvent with circulation, although the amount of solvent generated from the co-liquefaction process seems to equal the amount that is lost due to decomposition after about three circulations. Overall, it appears that the technique of solvent circulation is a viable prospect for this liquefaction process, although the apparent drop in solvent yield with increasing reaction time may necessitate that some portion of the circulating solvent be made of added gasoline or light oil.
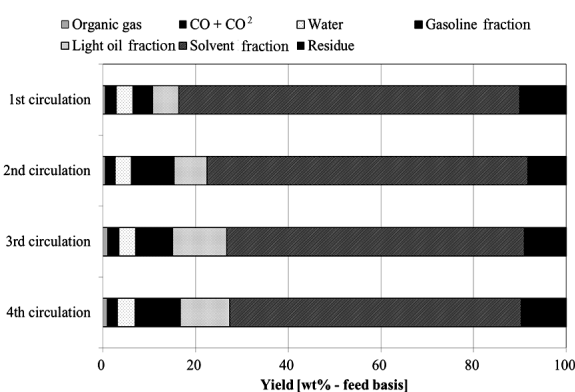

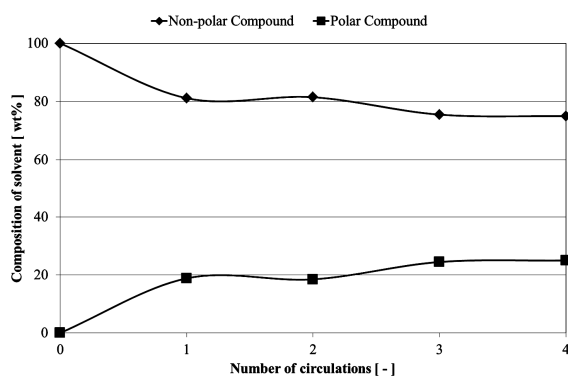Figure 4: Product yields obtained following co-liquefaction circulation trials
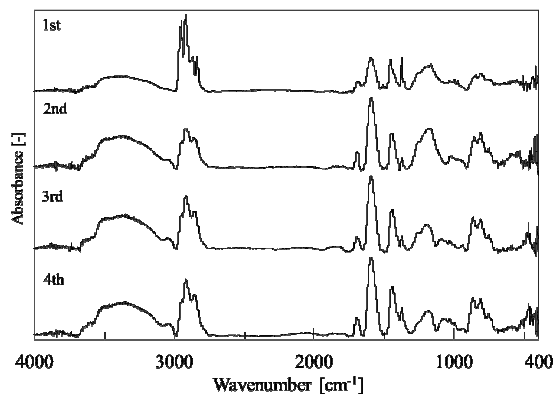

Figure 5: FT-IR spectra of residue materials resulting from circulation trials

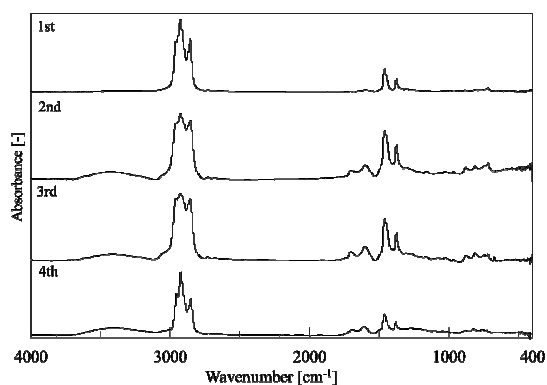Figure 6: Solvent compositions resulting from circulation trials

Figure 7: FT-IR spectra of polar compounds resulting from circulation trials
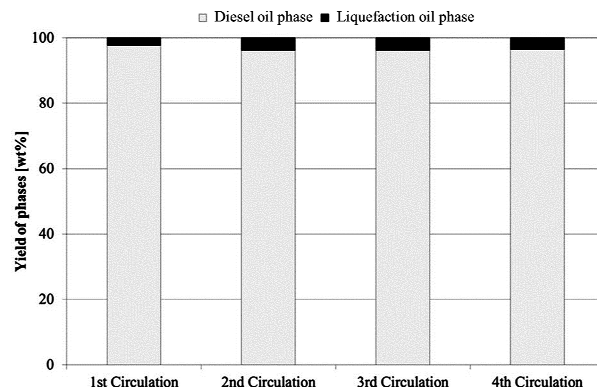
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Figure 8: Weight change of liquefaction oil phase and diesel oil phase in Diesel oil miscibility trials

Table 1
Physical properties of the liquefaction light oil fraction following the fourth circulation

	Liquefaction oil	Diesel fuel	Diesel fuel standard
Flash point (°C)	99	69	$\geqq$50
Pour point (°C)	-20	-15	$\geqq$-7.5
Cold filter plugging point (°C)	-27	-10	$\leqq$-5
Density (15 °C) [g/cm^3]	0.85	0.83	$\leqq$0.86
Kinematic viscosity (30 °C) [mm^2/s]	2.72	2.5	$\geqq$2.5

Fuel properties

We have assumed that the fuels produced by the liquefaction of cellulosic biomass would be mixed with diesel fuels originating from petroleum for the purpose of practical applications. However, problems with phase separation have been reported when biomass liquefaction fuels are mixed with diesel fuels in this manner.[4] The results of Diesel oil miscibility trials of mixtures of petroleum origin diesel fuel with the light oil fractions of liquefaction oil obtained following solvent circulation are summarized in Fig. 8. As can be seen, the two oils appear almost completely miscible though liquefaction oil and diesel oil were mixed in a weight ratio of 2 to 8. It should be noted that higher molecular weight alcohols were found in the liquefaction oil by GC-MS, presumably generated by reactions between the Japanese cedar and PP liquefaction products. We believe that these alcohols had a beneficial homogenizing effect on the mixture of the liquefaction oil and diesel fuel.

Data concerning the physical properties of the light oil fraction obtained from the solvent following the fourth circulation are given in Table 1. This table also contains data for typical diesel fuel, as well as the diesel fuel standards, for comparison purposes. The values shown here indicate that the liquefaction oil meets or exceeds the diesel fuel standard and that its physical properties are close to those of typical diesel fuel, confirming that the liquefaction oil may be applied as a diesel mixture fuel.

CONCLUSION

The effects of the co-liquefaction of cellulosic biomass (Japanese cedar) with a plastic (PP) have been investigated and the following results were obtained.

1) The Japanese cedar and PP liquefaction products react together to condense during the liquefaction process, reducing the formation of residue. At the same time, the cedar liquefaction products promote the decomposition of the PP.

2) The use of a solvent circulation process for the co-liquefaction of Japanese cedar biomass with PP appears viable.

3) The oil generated from the co-liquefaction of Japanese cedar with PP can be used as a light oil mixture fuel.

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