

Effect of Waste Type on Liquid Products Yields and Quality Obtained by Co-Liquefaction of Coal and Waste

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The need to find alternative liquid fuels more environmental friendly and with a more secure supply, has led to the idea of studying the conversion of carbonaceous wastes, like plastics, used tyres and biomass into liquid products to be used as fuels or as raw materials for several industries. As coal liquefaction is a well-known process to produce liquid products, coal blended with used tyres and plastic wastes was co-liquefied. Coal impregnated with 1 % wt. of molybdenum was used in co-liquefaction tests blended with 50 % wt. of used tyres or with the main plastics present in municipal solid wastes: PE (polyethylene), PP (polypropylene), PS (polystyrene) and a mixture of these plastics. The results obtained showed that all wastes promoted coal liquefaction. However, liquids yield and quality improved with the presence of plastics, while more solids were obtained when used tyres were used. Coal blends with PS wastes led to the highest liquid yield (74 % wt.) and conversion (88 % wt.) The presence of PE favoured the formation of linear alkanes, while PS promoted the formation of more aromatic compounds, which is in agreement with these plastics initial molecular structure. Some co-liquefaction tests were done in presence of tetralin, a hydrogen donor solvent that promoted the formation of liquids. Tetralin allowed increasing liquids yields obtained with plastics to values higher than 90 % wt., while in co-liquefaction of coal with used tyres led to liquids yields around 77 % wt.

1. Introduction

The transport sector has great contribution to CO₂ emissions and it is much dependent on petroleum derived fuels. Thus, it is imperative to find alternative liquid fuels more environmental friendly and with a more secure supply. Biofuels may play an important role in achieving both mentioned objectives, especially the decarbonisation of transport sector. However, biofuels may have negative impact, due to indirect land use, hence it is fundamental to find low indirect land use change (ILUC) risk biofuels. Another alternative is the use of wastes for liquid fuels production, which besides contributing to accomplish the mentioned objectives, also allows decreasing wastes accumulation.

Direct coal liquefaction (DCL) to produce mainly liquid products that may be used as fuels and/or as raw materials has been widely studied. Co-liquefaction of coal and wastes to produce liquid fuels and raw materials for different industries may be a suitable process in the near future, as coal has a longer lifetime than petroleum and has reserves not so concentrated in problematic areas. Co-liquefaction of coal and wastes has been less studied than DCL, though different types of wastes have been studied, including biomass, tyres and plastic wastes. Singh and Zondlo (2017) co-liquefied coal with untorrefied and torrefied biomass and found that the lignin content in torrefied biomass promoted coal liquefaction, because biomass degradation occurred at a lower temperature than coal. The effect of using coal mixed with waste tyres was studied by Khan et al. (2017) that reported that the maximum oil yield of 36 % was obtained for the blend 50:50 coal to waste tyres ratio. Good results were obtained by co-liquefaction of coal blended with PE (polyethylene), as these wastes are easier to

liquefy, promoting global mass and energy transfer and thus coal liquefaction and the formation of liquid hydrocarbons (Pinto et al., 2018). As the decrease of PE wastes content in coal blends led to liquid yield reduction, blends with 50 % wt. of PE in coal were selected (Pinto et al., 2018).

Molecular break-down occurs during coal liquefaction and thus the formation of radicals that need hydrogen to form stable compounds. Hydrogen may be supplied to the reaction medium by solvents with hydrogen donor capability or by molecular hydrogen. Some authors have studied the effect of using solvents with different hydrogen-donor capabilities on coal liquefaction. Frątczak et al. (2018) studied coal liquefaction with model-, petroleum- and waste-derived solvents: tetralin, 1-methylnaphthalene, light cycle oil (LCO), hydrotreated LCO, C9+ fraction, decalin and waste tyres pyrolysis oil. The best results were obtained when LCO was used in coal liquefaction. The use of waste tyres pyrolysis oil led to an increment in sulphur and nitrogen contents in liquid products and to a slightly lower amount of liquids. Niu et al. (2016) studied eight types of non-hydrogen-donor solvents in combination with tetralin that is a high hydrogen-donor solvent. The results obtained showed that the blends of tetralin with phenanthrene, pyrene, and fluoranthene improved coal conversion and oil yield compared with the use of only tetralin. These authors reported that solvents favoured coal liquefaction by supplying a medium for coal transport and heat transfer. The solvent may also act as a source to donate hydrogen and as a hydrogen shuttle between hydrogen and coal.

The main innovation of the work presented is the use of different types of wastes in co-liquefaction of coal, namely used tyres and the main plastics present in municipal solid wastes: PE, PP (polypropylene) and PS (polystyrene) were co-liquefied with coal, with the aim of improving coal liquefaction. Though the plastics and used tyres co-liquefied with coal might also have some capacity to supply hydrogen to reaction medium, some tests of co-liquefaction of coal with these wastes were also done in presence of tetralin with the aim of improving coal liquefaction and of increasing liquids yields.

2. Experimental part

Co-liquefaction tests of coal blended with wastes were done in a batch reactor, an autoclave made in Hasteloy C276 by Parr Instruments. The reactor was loaded with a mixture of brown coal with 50 % wt. of wastes: used tyres (in strips about 2 cm in length by 5 mm in width and 2 mm of thickness) and recycled plastics in pellets with sizes from 2 to 3 mm diameter: PE, PP, PS and a mixture of these three plastics (with 16.65 % wt. of each). Brown coal (BC) came from the Czechoslovak Army Mine (CSA) that is an opencast brown coal mine located in the North Bohemian Basin of the Czech Republic. Brown coal was impregnated with Mo (Mo (1 % wt.)/BC) by Soluciones Catalíticas Ibercat SL, as previous results showed that liquid formation was favoured (Pinto et al., 2018). In Table 1 are shown the proximate and ultimate analysis of the feedstocks used.

Table 1: Proximate and ultimate analysis of the feedstocks used in co-liquefaction.

	Proximate analysis (ar % wt.)				Ultimate analysis (daf % wt.)			
	Moisture	Ash	VM	FC ^b	C	H	N	S ^a
Coal	6.1	3.9	50.1	39.9	74.7	7.0	1.2	1.0
Recycled PE	0.0	0.1	99.8	0.1	85.7	14.3	0	0
Recycled PP	0.1	7.2	92.6	0.1	80.5	11.6	0.5	0.1
Recycled PS	0.3	0	99.5	0.2	86.1	7.4	6.1	0.1
Used tyres	2	2.9	61.6	33.5	86.1	7.2	0.2	1.5

VM: volatile matter; FC: fixed carbon; ar: as received basis; daf: dry and ash-free basis.

^aTotal sulphur. ^bBy difference.

After the autoclave was loaded with the blend of 50 % wt. of coal with waste, it was purged with nitrogen and pressurised with hydrogen to 3.45 MPa. Afterwards, it was heated and kept at 420 °C during 60 min. These experimental parameters were selected according to preliminary tests. Then, the autoclave was cooled down to room temperature and gases were collected, measured and the contents of CO, CO₂, H₂, CH₄ and other gaseous hydrocarbons, referred as C_nH_m (including alkanes and alkenes with carbon atoms from C₂ to C₄) were analysed by gas chromatography (GC). Solid and liquid products were weighted.

Liquid products directly collected from the autoclave were distilled according to ASTM D86 to obtain three fractions: the lighter one with a distillation temperature below 150 °C, the second fraction distilled in the range from 150 °C to 270 °C and the residual fraction had a distillation temperature beyond 270 °C. The first two distillates were analysed by GC and GC/MS (mass spectrometry). Solids were solvent extracted in a Soxhlet extractor, using n-hexane, toluene and tetrahydrofuran (THF) to determine the amount of liquids impregnated in solids. Total liquids yields were calculated considering the sum of the liquids directly retrieved from the autoclave and the liquids extracted from the solid product.

To assure that the reproducibility deviation of experimental results were below 5 %, at least two sets of runs were repeated at the same experimental conditions.

3. Results and discussion

3.1 Effect of solvent type on products yields and conversion

Coal (50 % wt.) was mixed with different types of the main plastics present in municipal solid wastes: PE, PP, PS and a mixture with equal amounts of these three plastics. In Figure 1 is shown the effect of the type of waste mixed with coal on products yields obtained by co-liquefaction. The total liquids presented in Figure 1 include direct liquids retrieved from the autoclave plus the liquids extracted from the solid product by solvent extraction, using n-hexane, toluene and tetrahydrofuran. The water obtained from the coal moisture and the water released by decarbonylation and hydrodeoxygenation reactions was not included in liquid yields and results are presented on % daf (dry and ash free coal).

When only PE was tested, the conversion of this plastic into liquid products was around 89 % wt., while co-liquefaction of coal blended with 50 % wt. of PE only led to liquid yield around 50 % wt., which shows that coal liquefaction is more difficult than PE. The presence of plastics is expected to be beneficial for coal liquefaction by favouring mass and energy transfer processes.

The highest liquid yield was obtained with PS wastes, being followed by the mixture of the three type plastic. The lowest liquid yield was obtained with PE, while PP led to liquids yield in between. PP also led to the highest gases yield, while the lowest amount of gases was obtained with PS. Total conversion obtained with PS was only 6 % higher than that obtained with PP. PE led to the highest solids content, this value was around 30 % higher than those obtained by other plastics. However, in general, it is possible to substitute one of the tested plastics by another one, or by a mixture. An adjustment of experimental conditions may lead to similar results. Only the presence of higher amounts of PE will lead to lower liquids yields and feedstock conversion.

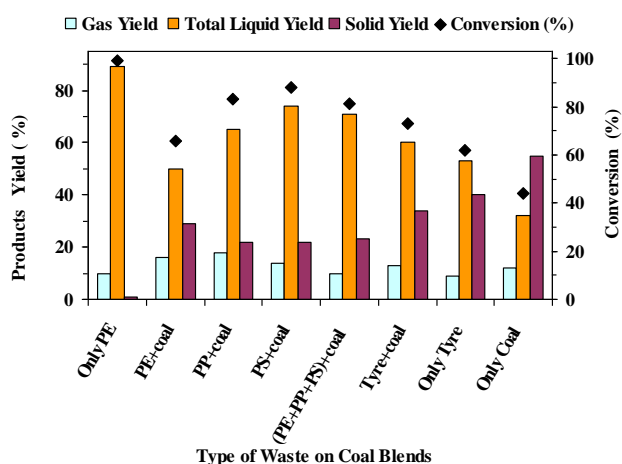


Figure 1: Effect of the type of waste on co-liquefaction conversion and products yields (without solvent). Experimental conditions: temperature - 420 °C, initial pressure – 3.4 MPa, reaction time - 60 min.

Liquid yield was around 53 % wt., when only used tyres were tested, this value was lower than that obtained by co-liquefaction of coal mixed with used tyres. Co-liquefaction of coal and tyres also allowed increasing the production of gases and reduced the solids obtained by coal liquefaction. On contrast to what was observed with plastics, co-liquefaction of coal and used tyres seems to have promoted the formation of liquids.

The addition of solvents with hydrogen donor capability to co-liquefaction processes, promotes the formation of stable molecules from the radicals formed by molecular break-down. Former co-liquefaction studies have shown that tetralin is a solvent with high hydrogen-donor ability (Pinto et al., 2018). Therefore, some co-liquefaction tests were also done in presence of tetralin, keeping constant all the other experimental conditions. The results presented in Figure 2 show that the addition of tetralin increased liquids yields and feedstocks total conversion, especially for the mixture of coal and PE, due to the relatively lower liquids yield and conversion. In presence of tetralin no great differences were obtained in liquids yields and conversion when one type of plastic was substituted by another, including the mixture of plastic wastes. In fact, liquids yields were higher than 90 % wt. and conversion were near 100 % wt. for all the plastic wastes tested.

The presence of tetralin in co-liquefaction of coal and used tyres allowed increasing liquids yields and conversion of around 27 % and 23 %. However, both parameters were lower than those obtained by co-liquefaction of coal and plastic wastes, probably because plastics are easier to liquefy than used tyres.

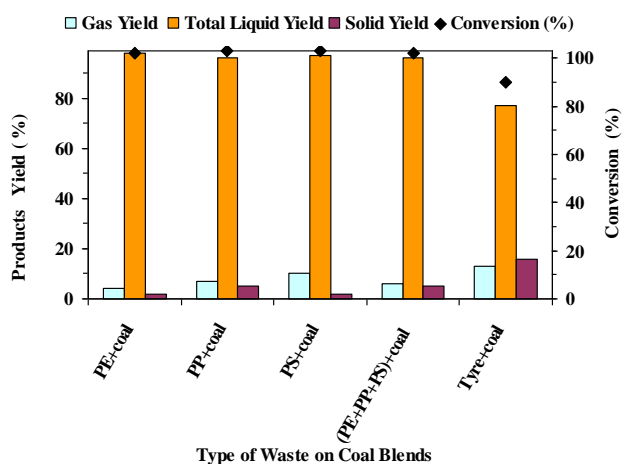


Figure 2: Effect of the type of waste on co-liquefaction conversion and products yields in presence of tetralin. Experimental conditions: temperature - 420 °C, initial pressure - 3.4 MPa, reaction time - 60 min, feedstock/tetralin ratio - 2.5.

In Figure 3 are presented the composition of gases produced by the different types of wastes tested. For all feedstocks tested, CO content was very low and gaseous hydrocarbons content decreased with the rise of carbon atom, thus CH₄ was the hydrocarbon formed with the highest content, while C₄ compounds showed the lowest contents. Hence, CH₄/C_nH_m ratio was around 1 for most situations, as CH₄ and C_nH_m contents were similar. In presence of tetralin, hydrogen consumption was lower than that in absence of this solvent, thus as there was more hydrogen in the final gaseous phase, the gases formed were more diluted in hydrogen and the contents of all other gaseous compounds were lower. In presence of tetralin CO content was also very small for all tests. In generally, CH₄/C_nH_m ratios were a little higher between 1.5 and 2.

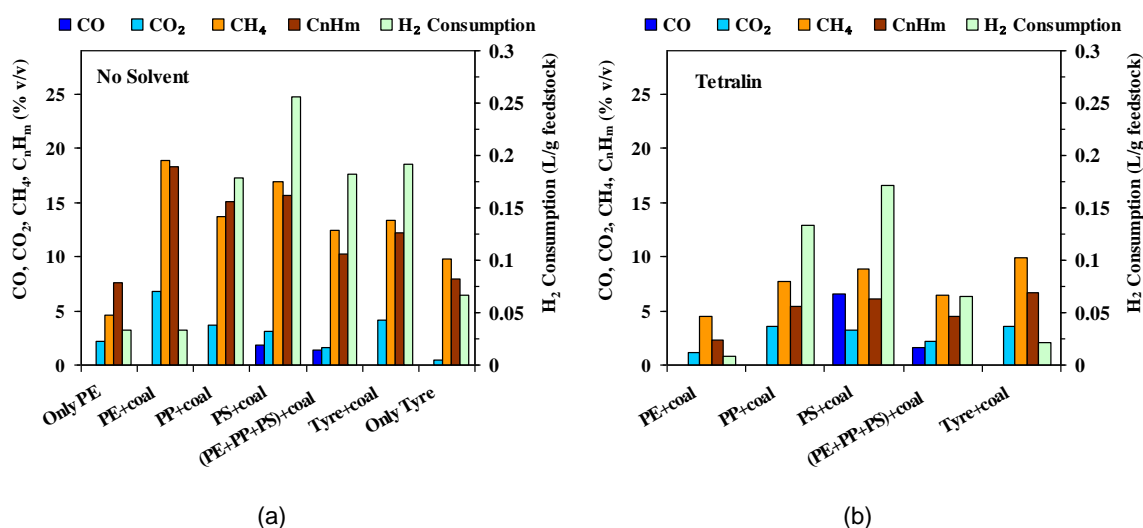


Figure 3: Effect of type of waste in coal blends on gas composition obtained by co-liquefaction of coal and wastes. (a) Without solvent and (b) In presence of tetralin. Experimental conditions as in Figure 2.

In absence of tetralin, hydrogen consumption was the highest when PS was used, which agrees with the highest content of liquids. When PE was blended with coal, hydrogen consumption was the lowest, which is in

accordance with the lower liquid yields and conversion. The results obtained seem to show that the presence of plastic in coal-liquefaction might also have contributed to supply some hydrogen to the reaction medium, as plastics molecular break-down might have led to the release of some hydrogen, which might be used for the stabilisation of the lighter radicals formed.

As expected, when tetralin was present in the reaction medium, the consumption of molecular hydrogen was lower, because of tetralin capacity to donor hydrogen to reaction medium. The reductions in molecular hydrogen consumption were between 80 and 25 %, depending on feedstock composition. In presence of tetralin the highest consumption of molecular hydrogen was obtained for the feedstock containing 50 % wt. of PS and the second highest consumption corresponds to the use of PP, while the lowest molecular hydrogen consumption was obtained for the use of PE in coal blends. These results agree with the molecular structure of the plastics tested. PS monomer (C_8H_8) contains an aromatic ring, PP monomer is the alkene C_3H_6 , while PE monomer is ethene (C_2H_4). Thus, it is expected that the breakdown of the aromatic rings of PS will need more hydrogen to be converted into stable compounds. The higher consumption of molecular hydrogen also agree with the higher liquids yields, that is to say the feedstocks that led to higher liquid yields presented higher consumption of molecular hydrogen.

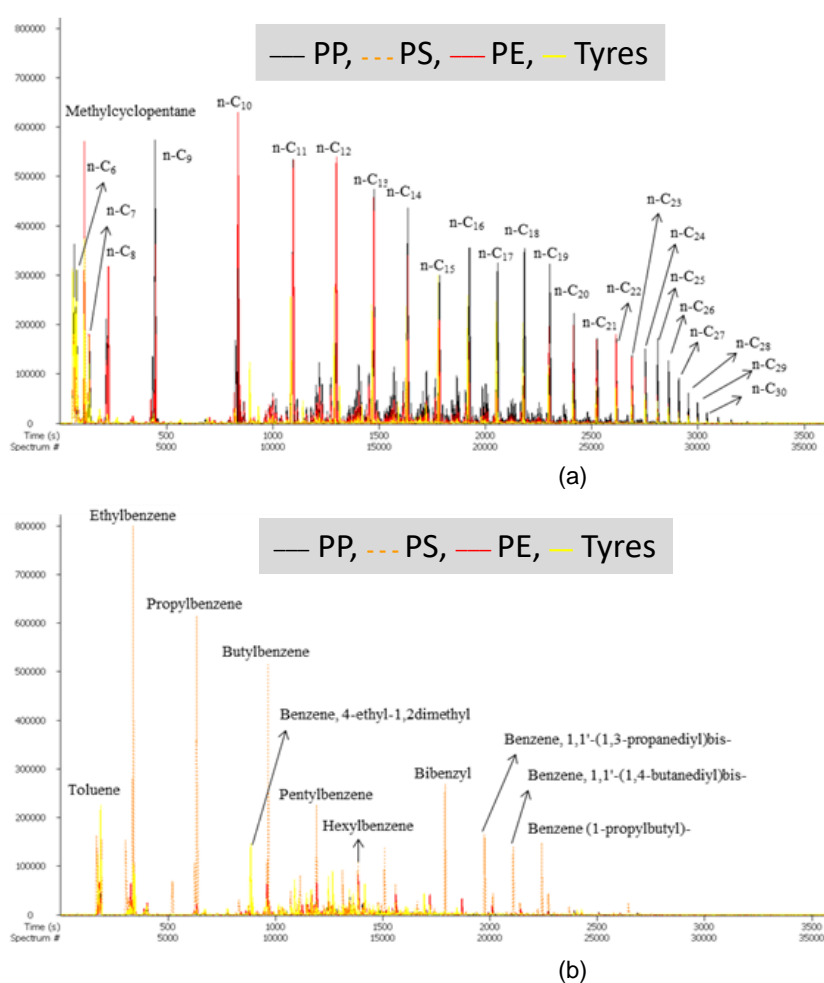


Figure 4: GC-MS analysis of liquids obtained by co-liquefaction of 50:50 blend of coal and wastes. (a) Alkanes and alkenes and (b) Aromatic compounds.

The determination of liquids composition is a difficult issue, because of the huge amount of compounds formed, most of them in small contents. In presence of tetralin this task is even more difficult, because the liquid compounds formed are much diluted and some of them are due to tetralin decomposition. Part of tetralin was transformed into naphthalene, because each tetralin molecular may supply 4 hydrogen atoms to the reaction medium. Though the formation of decalin is not suitable, as it corresponds to the consumption of hydrogen, decalin was also detected, but in lower content than naphthalene. Though a wide range of compounds was analysed, Figure 4, it was possible to observe that liquid hydrocarbons composition was dependent on the type

of plastic waste blended with coal. In general the dominant compounds were n-alkanes, branched alkanes were found in much smaller concentrations. Alkanes till C₃₂ were detected, while alkenes varied from C₁₀ to C₁₇. Though the names of alkenes are not written in Figure 4(a), to avoid lack of readability, they were detected, always near the correspondent alkane. The highest alkanes content was obtained in presence of PE, which suggests that alkanes formation was favoured by PE. On the other hand, the use of PP promoted the formation of alkenes. Probably, because the presence of the methyl group on the PP polymeric structure favoured the stabilisation of the intermediate radicals by the formation of a double bond. When PS was used, the aromatic content of liquid products increased, while the lowest alkanes and alkenes percentages were obtained. Ethylbenzene, propylbenzene, butylbenzene and toluene were the main compounds of the aromatic fraction. This seems to show that in presence of PS the experimental conditions used did not favour the cracking of all aromatic rings. Thus, the C – C bonds seems to be weak enough to be broken, which was followed by some rearrangement. Used tyres led to lower aromatics than PS, to lower alkanes than PE and with lower molecular weight. Some heavier compounds were also identified, probably predominately derived from coal, like: long series of alkylbenzenes, including trimethylbenzenes, naphthalene, methyl, dimethyl, and trimethylnaphthalenes, but in lower concentrations than the alkylbenzenes, and small contents of alkylphenanthrenes. Due to the complexity of liquids analyses, as several liquid fractions have to be analysed (3 distillation fractions plus 3 more fractions from solids solvent extraction with hexane, toluene and THF), liquids complete analysis is still in progress.

4. Conclusions

Co-liquefaction of coal mixed with plastics wastes is a good option, as plastics favoured coal conversion and the formation of liquid products, because plastics are easier to liquefy and thus mass and energy transfer were easier. Moreover, plastics may also supply some hydrogen to reaction medium, due to break-down reactions. The highest liquid yield and conversion were obtained with PS wastes, while PE led to the lowest values. However, the results obtained showed that, in general, it is possible to substitute one plastic waste by another, or by a mixture of them, probably an adjustment of experimental conditions would allow decreasing the differences observed in liquids and gases yields. Co-liquefaction of coal blended with used tyres was beneficial as higher liquids yields and conversion were obtained than the values when only one of these feedstocks was used. Though, no great differences were obtained in gaseous composition produced by different plastic wastes, the liquids produced were affected. The presence of PP led to the production of more alkenes, while PS favoured the formation of aromatic compounds. This is in agreement with plastics molecular composition. Tetralin improved co-liquefaction, as its conversion into naphthalene supplied hydrogen to the reaction medium, thus liquid yields was observed to increase. In presence of tetralin, molecular hydrogen consumption was lower than that obtained with no added solvent, thus lower hydrogen pressures may be used.

Acknowledgments

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