

Co-Liquefaction of Wastes and Coal Mixtures to Produce Added Value Liquid Compounds

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Nowadays there is an increasing need to find alternative fuels to reduce the dependency on imported ones and to decrease the negative environmental impact of wastes accumulation. Plastics are an important components of urban biowaste, thus their conversion into liquid fuels, in mixtures with other solid fuels still remains an important research goal. After the large experience obtained from coal gasification, it was found that co-liquefaction of coal and wastes may be a good solution to produce liquid fuels and raw materials for several industries. Co-liquefaction of coal blended with biomass gave unfavourable results, but co-liquefaction of coal mixed with PE (polyethylene) wastes led to encouraging results. The results obtained showed that the rise of PE content in coal blends led to an increase in liquid yield. As the main objective was the formation of liquid products, the mixture of coal with 50 wt% of PE was selected, as substantial total liquid yields were obtained, while using significant coal content. This blend was used to study the effect of initial hydrogen pressure, reaction temperature and time on products yields, using Response Surface Methodology (RSM) approach. Liquid yields were most affected by reaction temperature and pressure. The rise of temperature decreased liquid yields, while pressure had a positive effect, but the interaction between these two parameters showed a negative influence. Theoretical equations were used to calculate total and direct liquids yield (% daf). Total liquids are the sum of the liquids directly recovered from the autoclave (direct liquids) and the liquids extracted from the solid product. Both the theoretical model and the experimental results showed that the highest total liquids yields were obtained at 380 °C, 1.4 MPa and 90 minutes.

1. Introduction

The modern world needs huge quantities of energy, including fuels for transportation, heating, power generation, etc. Traditionally these fuels are generally derived from petroleum and other fossil sources. But the diminishing of their reserves, which ultimately increases the price of the commodities, coupled with environmental concerns resulting from their use, have led to the need of exploring alternative sources of energy and fuels (Pinto et al., 2013). Co-liquefaction of wastes and coal to produce liquid fuels and raw materials for several industries may help to fulfil these objectives.

Due to the decrease of petroleum reserves, there is an increasing interest in using direct coal liquefaction (DCL) to produce liquid fuels, as coal reserves are much bigger than petroleum ones (You, 2017). However, as coal may have significant amounts of sulphur, nitrogen, chlorine and heavy metals, the use of coal is not environmental beneficial. Co-liquefaction of coal and wastes blends, namely biomass and plastics, may also reduce coal negative environmental bearing (Li et al., 2016), allowing coal conversion into a clean fuel through liquefaction (Singh and Zondlo, 2016) and thus the use of coal to substitute petroleum (Trautmann et al., 2015).

During liquefaction, coal and wastes macromolecules are broken down and the radicals formed need hydrogen to originate smaller molecular structures. DCL needs high temperature and hydrogen pressure since coal H/C ratio is smaller than that of petroleum (Barraza et al., 2016). Co-liquefaction leads to the formation of

gases, solids and liquids products at room temperature. Gases are mainly formed by carbon monoxide and dioxide, hydrogen and C₁ to C₄ hydrocarbons (alkanes and alkenes), which may be used as fuel. Solid fraction (char) is a carbonaceous residue mainly composed by elemental carbon and result from the thermal decomposition of unconverted organic compounds. The solids produced by DCL can also be utilized in other processes, such as slurries for gasification (Dongmei et al., 2015). However, the main products are liquids to be used as fuels or as raw materials for several industries. These liquids are a complex mixture of organic compounds which may be grouped into alkanes, alkenes, aromatics and oxygenated compounds.

The main objective of the present study was to maximize liquid production through co-liquefaction of coal and wastes blends in the presence of gaseous hydrogen medium. Coal and biomass co-liquefaction tests did not lead to encouraging results, as coal liquefaction was not favoured by biomass presence. Besides bio-oils produced from biomass have some undesirable properties, namely: chemical instability, high solids content, ashes, oxygenated compounds and water, which prevent its direct use in conventional engines. On the other hand, the use of plastics favoured coal liquefaction. Pyrolysis of polyethylene (PE) produced around 85 wt% of liquid hydrocarbons containing a complex mixture of hydrocarbons from C₅ to C₂₀ (without the mentioned undesirable properties of bio-oils obtained from biomass). Around 5 wt% of gases and lower amount of solids were also produced. Thus, further tests of co-liquefaction of coal and wastes were done using PE as waste.

As PE wastes are easier to convert into liquids than coal, it was first analysed the effect of PE contents in coal co-liquefaction. The evaluation of possible synergism between coal and PE wastes is an important issue to be studied. The rate and extent of conversion of these feedstocks into liquid products also depend on operating conditions, thus the three more important experimental variables (reaction temperature, initial hydrogen pressure and reaction time) were optimized using Response Surface Methodology (RSM) approach. Previous works have shown that this methodology is a good process optimisation with a reduced number of experiments (Pinto et al., 2013). RSM methodology is also beneficial to supply information for optimisation of the experimental conditions that maximize the production of pre-defined gaseous and liquids compounds.

2. Experimental

2.1 Materials

The materials used in this study were a brown coal from the CSA mine in Czech Republic and PE wastes. Table 1 shows the proximate and ultimate analysis of the materials used.

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

| | Proximate analysis (as received wt%) | | | | Ultimate analysis (dry and ash-free wt%) | | | | |
|------|--------------------------------------|-----|-----------|---------------------------|--|------|-----|----------------|----------------|
| | Moisture | Ash | Volatiles | Fixed Carbon ^a | C | H | N | S ^a | O ^a |
| Coal | 6.1 | 3.9 | 50.1 | 39.9 | 74.7 | 7.0 | 1.2 | 1.0 | 16.1 |
| PE | 0.0 | 0.1 | 99.8 | 0.1 | 85.7 | 14.3 | 0 | 0 | 0 |

^a By difference.

2.2 Co-liquefaction procedure

The experimental trials were performed in a 1 L Hasteloy C276 autoclave made by Parr Instruments. The autoclave was first loaded with the feedstock mixture to be tested. It was purged with nitrogen and pressurised to the pre-set value of hydrogen. Then, it was heated and kept at the reaction temperature during the reaction time previously settled. At the end of the reaction time, the autoclave was cooled down to room temperature and gases were measured, collected and analysed by gas chromatography (GC) to determine the contents of CO, CO₂, H₂, CH₄ and other gaseous hydrocarbons. Solid and liquid products were weighted.

The liquid products directly recovered from the autoclave (named as direct liquids) were distilled according to ASTM D86 to yield three fractions: the lighter one distilled 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 (MS - mass spectrometry). The distillation curve of the liquid fraction was also compared to those of gasoline and diesel. Solids were extracted in a Soxhlet extractor, sequentially with n-hexane, toluene and tetrahydrofuran to determine the amount of liquids impregnated in solids. Total liquids are the sum of the liquids directly retrieved from the autoclave (direct liquids) and the liquids extracted from the solid product.

To assure that the reproducibility of experimental results were not higher than 5 %, at least two sets of runs were done at the same experimental conditions.

2.3 RSM methodology

RSM methodology was carried out to obtain a model for the yield of the total and direct liquids obtained by direct liquefaction of coal. It was decided to use a Cubic Centred Faces experimental plan due to the pressure and temperature limits of the equipment. The three experimental variables were x_1 : reaction temperature, x_2 : reaction time and x_3 : initial H_2 pressure. Table 2 shows the range of the experimental conditions.

Table 2: Range of experimental conditions.

| Level | | Temperature (°C) | Time (min) | Pressure (MPa) |
|--------|----|------------------|------------|----------------|
| Low | -1 | 380 | 20 | 1.4 |
| Medium | 0 | 415 | 55 | 2.4 |
| High | 1 | 450 | 90 | 3.4 |

The low, medium and high levels of these variables (-1, 0 and 1) were tested according to Table 3. The five repetitions of the central point (0, 0, 0) allowed to estimate the repeatability of the experiments.

Table 3: Low, medium and high levels of the X_i variables (-1, 0 and 1) tested.

| X_1 | X_2 | X_3 | Temperature (°C) | Time (min) | Pressure (MPa) |
|-------|-------|-------|------------------|------------|----------------|
| -1 | -1 | -1 | 380 | 20 | 1.4 |
| 1 | -1 | -1 | 450 | 20 | 1.4 |
| -1 | 1 | -1 | 380 | 90 | 1.4 |
| 1 | 1 | -1 | 450 | 90 | 1.4 |
| -1 | -1 | 1 | 380 | 20 | 3.4 |
| 1 | -1 | 1 | 450 | 20 | 3.4 |
| -1 | 1 | 1 | 380 | 90 | 3.4 |
| 1 | 1 | 1 | 450 | 90 | 3.4 |
| -1 | 0 | 0 | 380 | 55 | 2.4 |
| 1 | 0 | 0 | 450 | 55 | 2.4 |
| 0 | -1 | 0 | 415 | 20 | 2.4 |
| 0 | 1 | 0 | 415 | 90 | 2.4 |
| 0 | 0 | -1 | 415 | 55 | 1.4 |
| 0 | 0 | 1 | 415 | 55 | 3.4 |
| 0 | 0 | 0 | 415 | 55 | 2.4 |
| 0 | 0 | 0 | 415 | 55 | 2.4 |
| 0 | 0 | 0 | 415 | 55 | 2.4 |
| 0 | 0 | 0 | 415 | 55 | 2.4 |
| 0 | 0 | 0 | 415 | 55 | 2.4 |

3. Results and Discussion

3.1 Effect of PE contents in coal co-liquefaction

It was first studied the effect of the amount of waste plastic (PE) in coal blends on the production of liquids. These tests also allowed determining the best ways to operate the experimental installation, to recover the products and to perform their analysis. Coal contents in the blends changed from 0 to 80 wt% (Figure 1). Though it was possible to produce direct liquids at most conditions, solids extraction with solvents considerably increased the total liquids yields, as solids obtained after coal liquefactions trials were fully impregnated with liquids. Hexane was the solvent that achieved the highest extraction of liquids, while the liquids quantities extracted by either toluene or tetrahydrofuran were much smaller. The water produced in each trial, due to coal moisture and to reactions that release water (decarbonylation and hydrodeoxygenation)

was considered in liquids yield calculation. The rise of coal content in PE blends led to a decrease in liquid yield, both total and direct, and to an increase in solids (Figure 1). As the main objective was the formation of liquid products, the mixture of coal with 50 wt% of plastic was selected for further studies, as substantial total liquid yields were obtained, while using significant coal content, as shown in Figure 1. In the next step, the effect of reaction temperature and time and of initial hydrogen pressure on liquid yields, using RSM approach, was studied.

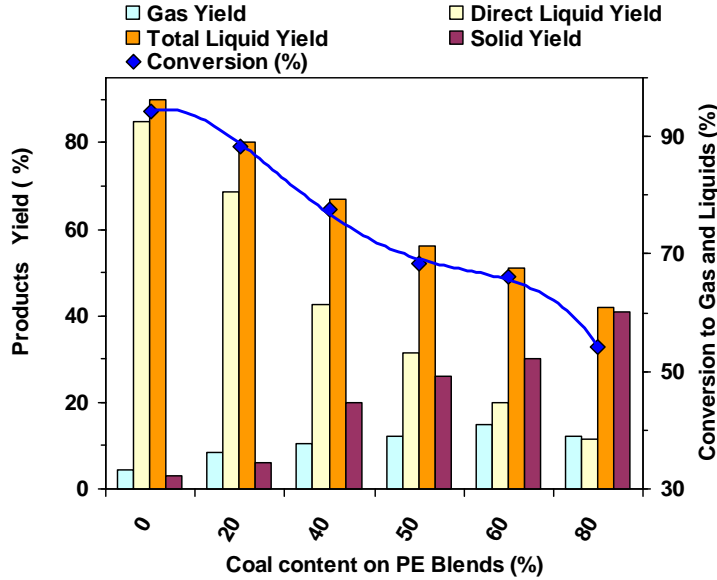


Figure 1: Coal direct liquefaction yields versus the coal content of the mixture.

3.2 Optimisation of coal co-liquefaction by RSM approach

Experiments were carried out to assess the relative influence of the three natural variables: x_1 , x_2 and x_3 , according to Table 3 data, to obtain the system response for the dependent variable (liquid yield). A second order polynomial model was fitted to the experimental results, using the least squares method. This model accounts for the influence of the individual parameters, as well as their interactions. Equation (1) is the modelling equation derived for the total liquids obtained. The correlation coefficient obtained was 0.939.

$$\begin{aligned} \text{Total Liquids (\% daf)} = & 54.8 - 15.9x_1 - 4.0x_2 + 6.2x_3 - 1.5x_1x_2 - 3.5x_1x_3 - 1.0x_2x_3 \\ & + 1.8x_1x_2x_3 + 0.7x_1^2 + 10.0x_2^2 - 9.0x_3^2 \end{aligned} \quad (1)$$

For the liquids directly retrieved from the reactor the following model was obtained by Eq (2).

$$\begin{aligned} \text{Direct Liquids (\% daf)} = & 20.0 - 2.0x_1 + 3.5x_2 - 0.1x_3 - 4.9x_1x_2 + 6.5x_1x_3 - 1.6x_2x_3 + \\ & 4.9x_1x_2x_3 - 10.8x_1^2 + 0.8x_2^2 - 0.1x_3^2 \end{aligned} \quad (2)$$

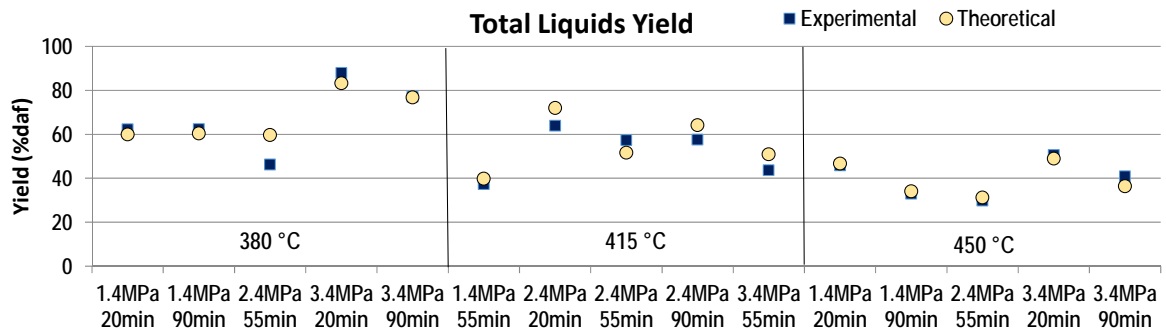


Figure 2: Experimental and theoretical yields for the total liquids.

Theoretical direct liquids yields (% daf) were calculated by equation (2). Theoretical and experimental liquids yields were compared. In Figure 2 is shown the comparison between the experimental and theoretical values for the total liquids production. A similar figure was drawn for direct liquids yields.

Due to the difficulty of 3D graphic representation of the three factors, the liquid production profile is shown for the variation of two factors, whilst the third one was kept constant. The use of RSM results supply a significant amount of information, as well as in a large number of plots, which cannot all be presented. Thus, in Figure 3 are presented an example of response surfaces derived from the second order model. In this case, it shows the influence of the reaction time on total liquids yield at the studied range of pressure and temperature values. Temperature and pressure were chosen because they showed high interaction. Similar plots were also drawn to analyse the other interactions of these parameters.

Figure 3 shows that the highest total liquid yields were obtained for lower temperatures and higher initial H₂ pressure. The rise of reaction time decreased the total liquid yields till the reaction time of 55 minutes, at which the lowest total liquid yield was obtained. However, further increases of reaction time, from 55 to 90 minutes, increased the total liquid yields.

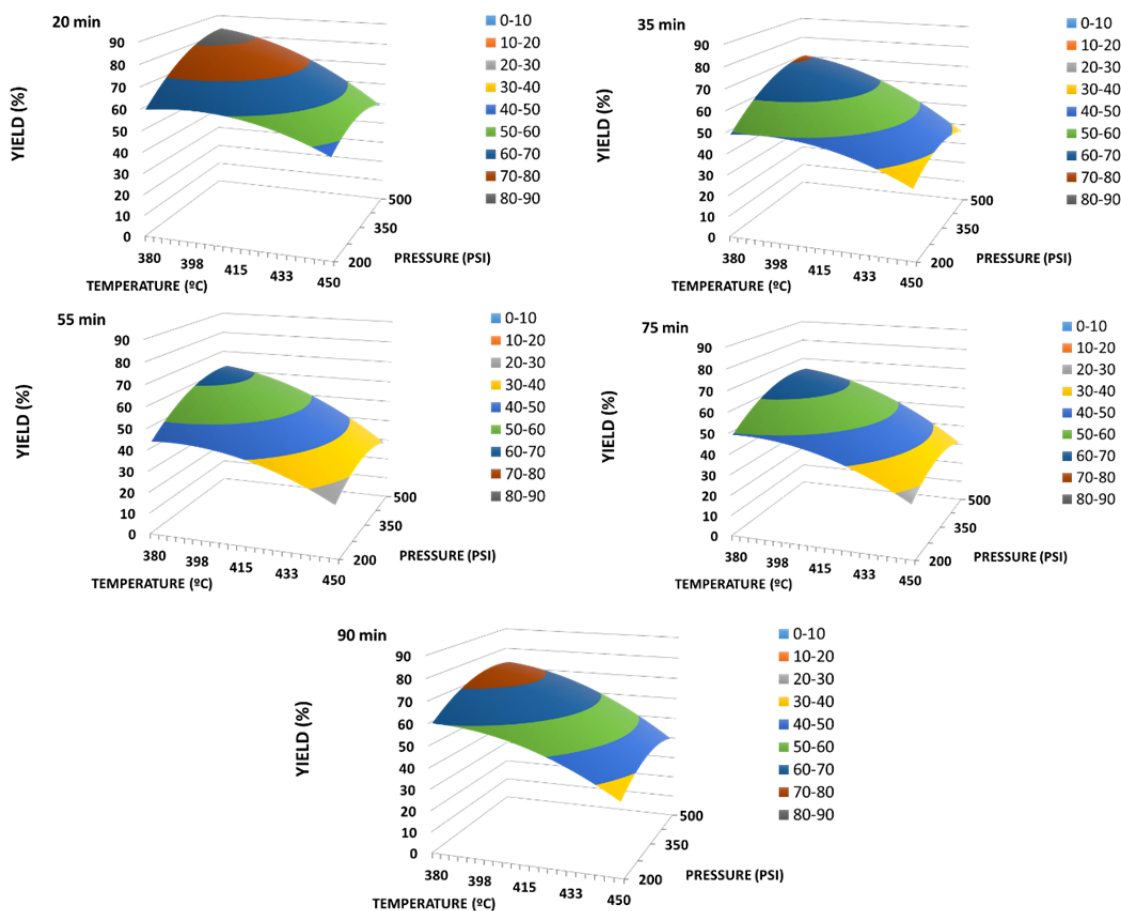


Figure 3: Examples of response surfaces obtained with the second order model for the total liquids. Yields presented refer to total liquid yields.

Similar plots may be drawn to analyse the other interactions of these parameters on direct liquids yield. The results obtained showed that the rise of reaction time increased the direct liquid yields, especially for lower temperatures and for lower initial H₂ pressure. For longer reaction times, the highest direct liquid yields are moved to lower temperatures and initial pressures.

The optimization of the liquefaction system was also carried out to maximize either the total liquids yield or the direct liquids yield. The optimal conditions were obtained by the maximization of equations 1 and 2, which corresponds to the highest values visually identified in the response surfaces graphics. The experimental conditions and the theoretical yields obtained are shown in Table 4. Experimental results fairly agreed with the theoretical ones for both direct and total liquid yields.

Table 4: Optimal experimental conditions as obtained by the maximization of the factorial design models.

| | Temperature (°C) | Time (min) | Pressure (MPa) | Theoretical yield (wt%) |
|----------------|------------------|------------|----------------|-------------------------|
| Total Liquids | 380 | 20 | 3.1 | 88 |
| Direct Liquids | 395 | 90 | 1.4 | 31 |

Gases GC analysis showed that the rise of coal in the blends co-liquefied led to an increase in CO and CO₂, especially CO₂ whose contents changed from 0.2 to 2.5 L/100g of feedstock. Hydrocarbons were also observed to increase. Alkanes contents were much higher than alkenes. CH₄ and C₂H₆ were the alkanes formed with the highest contents. The rise of carbon atoms led to a significant decrease in alkanes concentration.

GC-MS analysis for the direct liquids obtained from the 50% PE blend co-liquefied at 415 °C, 2.4 MPa and 55 minutes showed that the total ion chromatogram was dominated by n-alkanes with much smaller concentrations of branched alkanes arising from PE. However, the absence of alkenes arising from dehydrogenation indicates that some hydrogen transfer had occurred from the coal. The combined single ion chromatogram (SIC) for masses 91, 105, 120 indicated the presence of toluene (91), xylenes (120) and an extended series of alkylbenzenes, including trimethylbenzenes (120). The combined SICs for m/z 128, 142, 156 and 170 indicated that naphthalene, methyl, dimethyl, and trimethylnaphthalenes were present, but in lower concentrations than the alkylbenzenes. There were trace amounts of alkylphenanthrenes present and it is likely that these aromatic species have been derived predominately from the coal.

4. Conclusions

While the presence of biomass did not favoured coal liquefaction, the presence of PE showed a positive effect. The rise of PE content in coal blends favoured the formation of liquid yield. Thus, the mixture of coal with 50 wt% of plastic was chosen to optimise the main experimental conditions, namely: reaction temperature and time and initial hydrogen pressure.

Reaction temperature and pressure were the factors that presented the highest effect in liquid yields. Temperature presented a negative effect, while pressure a positive one, but the interaction between them presented a negative effect, which suggested the existence of a cross-effect.

Theoretical results showed a good adjustment with experimental ones for both direct and total liquid yields.

Optimized experimental conditions obtained by RSM led to the following conditions for total liquids yields (88 wt%): 380 °C, 3.1 MPa and 20 min, while for the direct production of liquids (31 wt%) the next conditions should be used: 395 °C, 1.4 MPa and 90min.

Acknowledgments

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