



## Coliquefaction of coal-plastic mixtures by two-stage methods

## Coliquefação de misturas de carvão-plástico por métodos de dois estágios

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### ABSTRACT

The two-stage co-processing of coal with medium-density polyethylene (MDPE) was investigated using ammonium tetrathiomolybdate (ATTM) as a catalyst. The first-stage plastic pyrolysis carried out at 420 °C, 6.0 MPa hydrogen pressure and HZSM-5 as catalyst. The second-stage coal and MDPE co-liquefaction had been performed in a hydroprocessing unit at 430 °C and 6.0 MPa hydrogen pressure with ATTM catalyst. A competitive experiment was performed by the way of one stage co-liquefaction of coal with MDPE using ATTM as catalyst and tetraline as solvent. The aim of the experiments was to determine the effect of the use of the waste plastic pyrolysis product as solvent. The results indicate that the hydroprocessed liquids of both the one stage and the two-stage co-processing of coal with MDPE have about 70% of compounds with boiling point below 350 °C, and meet the sulphur and nitrogen specifications for refinery feedstocks.

**Keywords:** plastics pyrolysis, two-stage co-liquefaction, medium-density polyethylene, waste plastic.

### RESUMO

O co-processamento em dois estágios do carvão com polietileno de média densidade (MDPE) foi investigado utilizando o tetratiomolibdato de amônio (ATTM) como catalisador. A pirólise plástica de primeiro estágio foi realizada a 420 °C, pressão de hidrogênio 6,0 MPa e HZSM-5 como catalisador. O segundo estágio de co-liquefação de carvão e MDPE havia sido realizado em uma unidade de hidroprocessamento a 430 °C e 6,0 MPa de pressão de hidrogênio



com catalisador ATTM. Um experimento competitivo foi realizado por meio da co-liquefação de um estágio de carvão com MDPE utilizando ATTM como catalisador e tetralina como solvente. O objetivo dos experimentos era determinar o efeito do uso do produto de pirólise de plástico residual como solvente. Os resultados indicam que os líquidos hidroprocessados de um estágio e de dois estágios de co-processamento de carvão com MDPE têm cerca de 70% de compostos com ponto de ebulição abaixo de 350 °C, e atendem às especificações de enxofre e nitrogênio para as matérias-primas de refinaria.

**Palavras-chave:** pirólise do plástico, co-liquefação em dois estágios, polietileno de média densidade, resíduos plásticos.

## 1 INTRODUCTION

In recent years, disposal of plastic wastes has become an increasingly serious environmental concern. Due to an ever increasing volume of plastic products, sanitary landfills can no longer continue to be the major means for plastic wastes disposal. Plastics recycling appears to be a possible alternative solution and has potential for high growth. In order to obtain distillate liquids or petroleum compatible refined products from coal, addition of hydrogen is necessary [1-3].

A possible method for hydrogen addition is co-processing of coal with polymeric waste materials since these latter materials contain hydrogen at levels much higher than are found in coal. The breakdown of waste rubber tires is interesting because the liquids derived may prove to be important as a coal dissolution and/or hydrogen donor solvent. Previous study shows that a solid acid catalyst (HZSM-5 zeolite) was highly active for the liquefaction of the plastics alone, typically giving oil yields of 80-95 % and total conversions of 90-100 % at temperatures of 430-450 °C [4-7].

Two-stage coal liquefaction offers the potential for significant improvement over single-stage processing [8-10]. The objective of this research was to determine the feasibility of using two-stage co-processing for coal and MDPE reaction systems. The plastics (mainly polyethylene and polystyrene) were thermal cracked to obtain liquid products according to the different weight ratio of polyethylene and polystyrene. The liquid products were used as solvent for the second stage of co-liquefaction of Xingyuan coal and MDPE. Investigated the



influence of the solvent which produced from the first stage by different weight ratio of polyethylene and polystyrene on the second stage of co-liquefaction of Xingyuan coal and MDPE. The results illustrate that there is an optimal weight ratio of polyethylene and polystyrene for the co-liquefaction of Xingyuan coal and MDPE.

## 2 EXPERIMENT SECTION

### 2.1 MATERIALS

The sample of Xingyuan coal obtained from Guizhou Xinsheng Coal Chemical Co., Ltd., and dried sample of Xingyuan coal was ground to < 100 mesh particles and used as a coal source. Table 1 lists the proximate and ultimate analyses of the coal. The proximate and ultimate analyses were all based on air dried basis.

Table 1 Proximate and ultimate analyses (wt %) of Xingyuan coal<sup>a</sup>

Proximate analysis			Ultimate analysis (daf)				S <sub>t,d</sub>
M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	C	H	N	O <sub>diff</sub>	
2.862	19.16	26.37	71.59	2.36	0.68	0.22	8.17

<sup>a</sup> diff, by difference; daf, dry and ash-free basis; M<sub>ad</sub> moisture (air-dried basis); A<sub>d</sub>, ash (dry basis); V<sub>daf</sub> volatile (dry and ash-free basis); and S<sub>t,d</sub>, total sulfur (dry basis)

Polyethylene and polystyrene were supplied as 3.0mm extruded pellets from Dongwan plastic Ltd. HZSM-5 and ATTM were purchased from Shanghai Shentan environmental protection new materials co., LTD. Pentane and tetrahydrofuran were purchased from Xiya reagent co., LTD.

### 2.2 PREPARATION OF MIXED SOLVENT WITH DIFFERENT WEIGHT RATIO OF POLYETHYLENE AND POLYSTYRENE

In the first stage reaction, the different weight ratio of polyethylene and polystyrene mixtures were liquefied in order to obtain a liquid product to be used as the solvent in the second stage co-processing reaction. Fixed the weight of polyethylene at 200 g, weighted 100 g, 200 g, 300 g, 400 g and 600 g polystyrene, respectively. To make the weight ratio of polyethylene and polystyrene at 2:1, 1:1, 1:1.5, 1:2 and 1:3.

The plastics mixtures were liquefied in a 1L magnetically stirred autoclave at



420 °C for 120 min under an initial H pressure of 6.0 MPa introduced at ambient temperature. The reactors were agitated vertically at 450 rpm.

The loading for the HZSM-5 catalysts was 5 wt. % on a plastics charge basis. After the reaction was completed, the reactor was quenched in ambient water. The liquid products were extracted with THF and then hexane, and the soluble amounts of each fraction were determined. The hexane solvent was evaporated from the hexane soluble liquid product, which was then used as the solvent for coal liquefaction in the second stage reaction.

### 2.3 CO-LIQUEFACTION OF XINGYUAN COAL AND MDPE USING THE LIQUID PRODUCT OF PYROLYSIS AS SOLVENT

The co-liquefaction experiments were conducted in 1L magnetically stirred autoclave which was shaken at 400 rpm at the desired temperature. Usually 1:1 weight ratio of MDPE + Xingyuan coal, five times of solvent (based on the total weight of MDPE and Xingyuan coal, the liquid product of pyrolysis which produced in the first stage), 5% weight ratio of ATTM (based on the total weight of MDPE and Xingyuan coal) were charged in the 1L magnetically stirred autoclave. The reaction times were 120 min. at 430 °C, and the atmosphere in the magnetically stirred autoclave was 6.0 Mpa cold H pressure.

After the reaction was over, the products were removed from the reactor with tetrahydrofuran (THF) and extracted in a Soxhlet apparatus. The THF solubles were subsequently separated into pentane soluble (Oil) and pentane insoluble (AS + PS) fractions. Total THF conversion was determined from the amount of insoluble material that remained (residue). Any added catalyst was subtracted from the residue sample weight.

There are totally 5 experiments, and they are designed as Two stage 1, Two stage 2, Two stage 3, Two stage 4 and Two stage 5, respectively.

### 2.4 CO-LIQUEFACTION OF XINGYUAN COAL AND MDPE USING TETRALINE AS SOLVENT

1:1 weight ratio of MDPE + Xingyuan coal, five times of tetraline solvent (based on the total weight of MDPE and Xingyuan coal), 5% weight ratio of ATTM



(based on the total weight of MDPE and Xingyuan coal) were charged in a 1L magnetically stirred autoclave. The autoclave was heated to 430 °C under 6.0 Mpa initial H<sub>2</sub> pressure, and maintained for 120 min under stirring at 500 RPM.

The products were divided into hexane soluble fraction as oil, the hexane insoluble-THF soluble fraction as asphaltene and preasphaltene (AS + PS), and THF insoluble fraction as residue. The experiment was designed as One stage 1.

## 2.5 MOLECULAR WEIGHT STUDIES

The M<sub>w</sub> and M<sub>n</sub> of oil and AS + PS obtained from Two stage 1, Two stage 3 and One stage 1 were measured in a UltiMate 3000 apparatus. Defining dispersivity (D) is M<sub>w</sub>/M<sub>n</sub>. D is an index for the homogeneity of the sample. All molecules of the sample have the same size when D = 1.0.

## 3 RESULTS AND DISCUSSION

### 3.1 OIL AND TOTAL CONVERSION OF CO-LIQUEFACTION OF COAL AND MDPE IN EACH EXPERIMENT

Figure 1. The oil and total conversion of co-liquefaction of Xingyuan coal and MDPE in each experimente

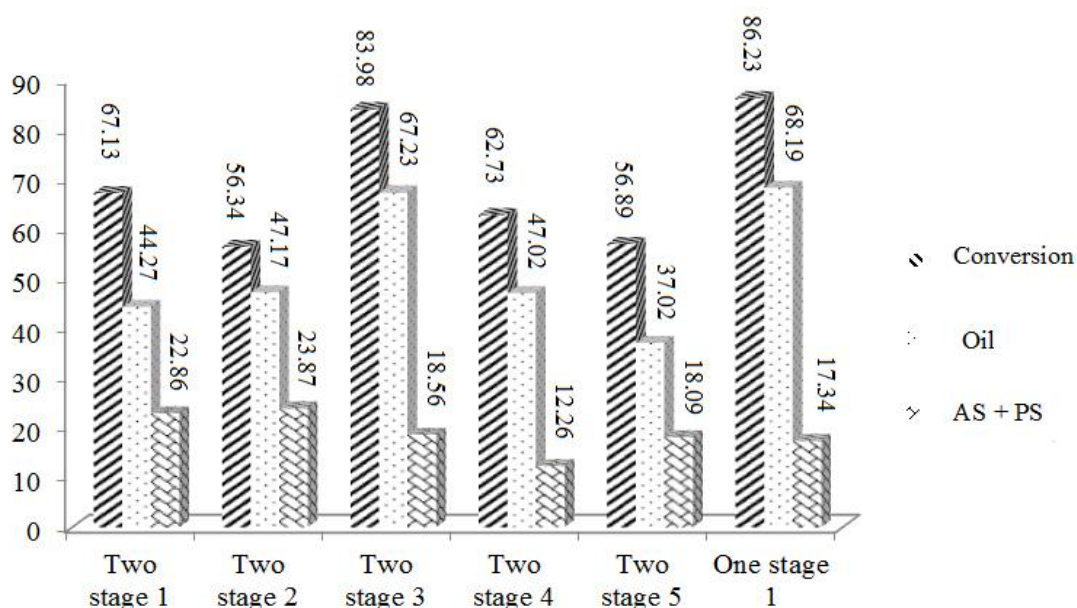




Figure 1 shows the oil and total conversion of co-liquefaction of coal and MDPE in each experiment. As for the two stage co-liquefaction experiments, the co-liquefaction of coal and waste plastic needs the kind of solvent that either consists of aliphatic hydrocarbon or aromatic hydrocarbon. The authors prepared mixed solvent which contains aliphatic hydrocarbon structure and aromatic hydrocarbon structure. The aromatic hydrocarbon plays the role of loading H atom at the reaction of co-liquefaction of coal and waste plastic. These new hydrogenizes aromatic hydrocarbon speeds the H atom transmission of coal pyrolysis, thus makes the total conversion of coal liquefaction improved greatly.

The 1:1.5 weight ratio of polyethylene and polystyrene as solvent achieves the highest oil yield for 1:1 weight ratio of MDPE and Xingyuan coal co-liquefaction.

It also can be seen from One stage 1 that when a strong H donor such as tetraline as solvent was used at co-liquefaction of coal and waste plastic, it gets high oil yield and total coal conversion. It evinces that high active hydrogen density is important for the co-liquefaction.

### 3.2 MOLECULAR WEIGHT DISTRIBUTION

The calculate results of the mass distribution of three products of liquefaction fractionated into oil, asphaltene and preasphaltene for Two stage 1, Two stage 3 and One stage 1 is shown in Table 2.



Table 2. Molecular weight data for liquid products obtained at 430 °C

	$M_n$	$M_w$	Dispersivity
Hexane soluble (Oil)			
Two stage 1	370	724	1.956
Two stage 3	300	430	1.433
One stage 1	278	380	1.366
Hexane insoluble-THF soluble (AS + PS)			
Two stage 1	480	997	2.07
Two stage 3	527	973	1.846
One stage 1	420	719	1.711
Overall molecular weight data <sup>a</sup>			
Two stage 1	273.5	548.4	2.005
Two stage 3	299.5	469.6	1.568
One stage 1	262.3	383.7	1.462

<sup>a</sup>Determined from data for individual fractions and the mass fraction data of Figure 1.

It is obviously that lower amounts of hexane insoluble-THF soluble compounds and higher quantities of the desirable lower molecular weight Hexane soluble fractions over the corresponding fraction of liquids that are obtained by processing either Two stage 3 or One stage 1. Similar enhancement in coal conversion and improvement in product quality were observed in the two experiments. The results indicates that Two stage co-liquefaction of waste plastic and coal using the liquid product of pyrolysis as solvent in the second stage results in the lowering of C/H ratios of the liquids obtained.

Whereas, the main reason for the mild condition of co-liquefaction of waste plastic and coal was the high H contribution of solvent. The paper prepared different ratio of solvent with aliphatic hydrocarbon and aromatic hydrocarbon to meet with the pyrolysis section of waste plastic and coal, thus synergetic effect of waste plastic and coal is happened, and the yield of oil improved. For co-liquefaction of MDPE and Xingyuan coal with 1:1 weight ratio, it is obviously that



the best solvent which produced in the first stage is the 1:1.5 weight ratio of polyethylene and polystyrene, as compared to the rest four experiments in 2.2. *Preparation of mixed solvent with different weight ratio of polyethylene and polystyrene*

#### **4 CONCLUSIONS**

1. Exploratory reaction studies have shown two-stage coal co-processing with waste plasticss to yield high conversions of coal (> 80 %) with a high selectivity for oil (> 60 %). the different ratio of aliphatic hydrocarbon and aromatic hydrocarbon were first thermally cracked in a first stage to yield a liquid solvent for the second-stage coal and MDPE co-processing.
2. New results for plastics liquefaction and coal-plastic co-liquefaction suggest that the nature of the plastic, the solvent, and the reaction atmosphere can all have a significant on product yields. A thorough experimental matrix is needed to explore this parameter space. Further catalyst development aimed at producing cheaper, more robust catalysts for coal-waste plastic co-liquefaction is required.

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