

Coliquefaction Studies of Waste Polymers and Lignite Influenced by Acidic and Oil-Soluble Catalysts

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ABSTRACT: A detailed study of postconsumer polymer coliquefaction with lignite influenced by two acidic and two oil-soluble catalyst precursors is presented in this article. The conversion of reacting solids into gaseous and liquid products was determined in four initial series of coprocessing experiments performed with and without catalysts on a suite of four heavy organic solvents. Based on the results obtained, two newer series of experiments were also designed and carried out, aimed at the optimization of this complex transformation using this time lignite oxidatively pretreated. It was found that the mentioned hydroconversion is a promising way of hydrocarbon synthesis and that oxidatively pretreated lignite proved superior to the raw material. It was also found that the oil-soluble catalysts employed indicated a particularly noticeable activity increase, influencing, thus, the efficacy of the conversions achieved. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1323–1330, 2000

Key words: coliquefaction; waste plastics; catalysts; organic solvents; lignite

INTRODUCTION

The development of attractive technological methods for industrial production of motor fuels and petrochemical feedstocks alternatively to petroleum and gas is an active area of scientific research nowadays.^{1–3} In view of that issue, this study was undertaken, exploiting the simultaneous waste polymers–coal coliquefaction, targeting the determination of viable process-suitable conditions.

The mentioned conversion can meet a wide range of processing objectives as it has the potential advantage of recycling a part of the enormous

amounts of post-consumer plastics our society generates, upgrading, simultaneously, coal-derived polyaromatic compounds. It must also be noticed that waste polymers consist of suitable-for-liquefaction molecular-chain structures with high hydrogen-to-carbon ratios. This last property is capable of increasing the hydrogen content of the coal-dissolution products and coincided with a decreased need for the addition of external hydrogen gas during the said reaction.^{3–5}

Coal liquefaction is believed to proceed through degradation to oily compounds and many factors including operating conditions, coal and polymer synergism, catalyst efficiency, and solvent properties influence this transformation. Although coal is characterized as a nonhomogenous solid with a complex molecular constitution, it is well documented that when it is heated a thermal

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cleavage of the weaker C—C bonds occurs initially.⁶ Stronger C—C bond splitting becomes possible, influenced by the solvent interaction.^{7–9} Then, adequate hydrogen addition may convert the former radicals to the desired light products with a high H/C ratio.^{7–9} Hence, it is concluded that a solvent's ability to transfer hydrogen and to solvate coal fragments is critical for this hydroliquefaction. In this work, four types of high boiling organic solvents were utilized, having the needed polynuclear aromatic compounds.^{10,11} They ranged from a petroleum residual liquid to a coal-derived solvent and also included two oils obtained by vacuum pyrolysis of waste plastics and rubbers.

Coal rank also emerges as a significant characteristic affecting closely its synergism with the various reaction parameters.^{12,13} In the present study, an attempt was made to investigate the preceding thermochemical conversion using lower-grade coal, for example, lignite. This choice can meet a wide range of processing objectives as it is postulated that lignitic macromolecules are not tightly bounded and the needed cleavages of the bridges linking molecules would be easier in comparison to higher ranks of coal, for example, anthracites or bituminous coals.^{14,15} In addition, a literature survey has shown that coals of lower rank have been evaluated in giving satisfactory reaction yields provided with high amounts of light distillates.^{16,17}

Apart from the coal itself, the role of catalyst employed is of primary interest as a catalytic action—proceeding through polyaromatic compounds bond cleavages—with enhanced yields obtained.¹⁸ In the recent literature, a variety of catalyst types were investigated for this coprocessing and many researchers through a series of studies obtained good conversion rates using metal chlorides, for example, CuCl_3 , MoCl_3 , and ZnCl_2 (ref. 19) or hydrocracking catalysts, for example, $\text{NiMo}/\text{Al}_2\text{O}_3$ or $\text{SiO}_2/\text{Al}_2\text{O}_3$.²⁰ In this work, the influence of two acidic and two oil-soluble catalyst precursors were examined to evaluate their effects on the efficiency of the mentioned hydrocracking–hydrogenation transformation.

In the present report, at first, the results of hydroprocessing experiments with and without catalysts are summarized, indicating the most active ones that promoted markedly waste plastics coliquefaction with lignite on a suite of four heavy organic solvents. Taking into consideration these initial findings, two newer series of experiments were designed aimed at maximization of

the yields obtained by using this time-upgraded lignite, for example, lignite oxidatively pretreated with H_2O_2 . In the first series with each solvent, the corresponding best-performing catalyst was used. In the second one, two successive stage runs of the precedent mixtures were undertaken, optimizing, thus, the process. The conversion of reacting solids into gaseous and liquid products and, in particular, into hexane- and tetrahydrofuran-soluble material, was determined. In addition, hexane solubles were separated by open-column chromatography into paraffinic, aromatic, and polar subfractions by selective adsorption on alumina and silica gel.^{21–23} Finally, the effects of catalysts, solvents, and, mainly, the conducted oxidative lignite treatment as a preliminary step on the product distribution obtained were investigated and serious observations concerning the interactions that occurred were outlined.

EXPERIMENTAL

The lignite sample from the Florina mine in Northern Greece was dried, ground to a –60 mesh screen, and stored. Its proximate analysis is presented in Table I. Table I also gives the characteristics of the individual postconsumer polymers used, for example, polystyrene (PS), polypropylene (PPE), and waste rubber tire (WRT). Waste plastics feed the reaction in the form of an equal parts' mixture consisting of PS, PPE, and WRT. Four commercial solvents were also employed in this study, for example, a heavy petroleum residue, a coal-derived solvent, and two oils produced by the vacuum pyrolysis of waste plastics and rubber tires. Their analyses are presented in Table II.

The catalyst precursors tested in the reaction runs were nickel naphthenate (Shepherd, Cincinnati, OH; denoted as NiN), iron naphthenate (Shepherd; denoted as FeN), and two zirconia-based acidic catalysts synthesized in our laboratory, for example, $\text{ZrO}_2/\text{Al}_2\text{O}_3$ (denoted as Zr 1) and $\text{ZrO}_2/\text{SiO}_2$ (denoted as Zr 2). Their preparation by a modified sol–gel method was described in detail previously.²⁴

One-hour experiments were performed in a 200-mL stainless-steel autoclave at a temperature of 420°C and included thermal and catalytic reactions of lignite with the mixture of waste plastics. During each thermal run, the autoclave was initially charged with 10 g of dry ash-free lignite, 10 g of postconsumer polymers, and 10 g

Table I Used Materials' Properties

	Lignite (Raw)	Lignite (Pretreated)	PS	PPE	WRT
Proximate analysis of lignite and postconsumer plastics (wt % as received)					
Volatile matter	48.53	54.23	98.32	97.80	63.04
Fixed carbon	27.41	32.82	0.72	0.96	29.60
Moisture	12.70	4.61	0.30	0.73	0.82
Ash	11.36	8.34	0.66	0.51	6.54
Ultimate analysis of lignite and postconsumer plastics (wt % daf)					
Carbon	65.80	69.34	91.80	85.57	84.02
Hydrogen	5.39	5.52	7.54	13.85	8.56
Nitrogen	2.49	1.91	0.15	0.46	0.63
Sulfur	1.34	0.83	0.07	0.04	1.89
Oxygen (by difference)	24.98	22.40	0.44	0.08	4.90

of a solvent. In the case of the catalytic experiments, 2 g of the catalyst was also added. The autoclave was then closed, purged sequentially with nitrogen and hydrogen, and then pressurized with hydrogen to an initial pressure of 800 psig at ambient temperature. Afterward, the reactor was brought to the desired temperature, being heated by an electric mantle. When the reaction period was completed, the autoclave was quenched to room temperature and depressurized, and the included gases and highly volatile compounds were collected in a stainless-steel gas trap.

Based on the results obtained so far, two newer series of coliquefactions were designed and undertaken, targeting maximization of the yields achieved by repeating the best-performing experiment of each of the four previous sets. It is noticeable that, this time, lignite pretreated appropriately was employed. Pretreatment consisted of lignite contact with a 12 wt % H_2O_2 aqueous solution for 1 h followed by water washing and froth flotation of the treated sample to collect the carbonaceous matrix and to separate all split impurities. The lignite analysis after the former procedure is depicted in Table I, proving that there was a reduction in moisture and ash content.

In each experiment of the first series, the autoclave was loaded with 10 g of dry ash-free pretreated lignite, 10 g of the waste plastics mixture, 10 g of solvent, and 2 g of the corresponding best-performing catalyst, for example, in petroleum residue, FeN was added; in coal-derived liquids, FeN; in waste plastics oil, Zr 1, and in waste tire oil, NiN. Then, the prescribed autoclave run procedure was followed. Afterward, coliquefactions in two stages were attempted. In each of these experiments, the autoclave was initially loaded with 10 g of the waste plastics mixture, 10 g of the solvent, and 2 g of the corresponding best-performing catalyst as previously described. The precedent autoclave run procedure was followed during the first stage. Then, 10 g of pretreated lignite was added into the autoclave for the second stage of the reaction; the gases collected during the first stage were also transferred from the gas trap into the autoclave. A similar, as previously mentioned, autoclave procedure followed and the gaseous and liquid products were collected at the end of the reaction period. Finally, the gaseous products of the reactions were determined by standard gas chromatographic methods²⁵ using a combination of flame ionization and thermal conductivity detectors. Hexane-soluble

Table II Solvents' Elemental Analysis (wt %)

	Petroleum Residue	Coal-Derived Solvent	Waste Plastics Oil	Waste Tire Oil
Carbon	86.5	89.4	88.0	90.5
Hydrogen	11.8	8.3	11.6	8.4
Sulfur	1.2	0.7	—	0.2

Table III Composition of the Gases Produced from the Last Series of Experiments (wt % of Gas)

	FeN + Petroleum Residue	FeN + Coal Liquid	Zr 1 + Plastics Pyrolysis Oil	NiN + Tire Pyrolysis Oil
Methane	6.7	5.2	5.3	4.6
Ethylene	14.0	11.8	12.6	11.7
Ethane	5.2	6.9	8.3	7.5
Propylene	10.4	11.3	9.5	14.3
Propane	7.9	8.9	7.0	8.2
iso-Butylene	1.8	0.6	2.1	1.5
<i>n</i> -Butane	3.6	2.2	3.4	2.8
iso-Butane	1.1	0.8	0.9	0.6
C ₅ ⁺	5.3	7.0	7.6	6.1
CO	15.2	14.1	16.7	15.4
CO ₂	11.4	9.5	10.2	12.3
H ₂ S	2.8	3.8	2.1	2.8
Unaccounted	14.6	17.9	14.3	12.2

products were also analyzed by open-column chromatography, disclosing their paraffinic, aromatic, and polar content by selective adsorption on neutral alumina and silica gel. The results are presented in Tables III and IV.

The gas yield was calculated by weighting the gas trap before and after venting the gases from it. The solid and liquid reaction products were removed from the reactor carefully and they were analyzed by solvent fractionation. Hexane was employed initially followed by tetrahydrofuran (THF) and the products were separated into oils (hexane soluble), asphaltenes (THF-soluble but hexane-insoluble), and THF-insoluble. The amounts of these fractions were determined and, finally, the total reactants' conversion was calculated using the equation $\text{conversion} = 100 - \% \text{ THF-insoluble}$, where $\% \text{ THF insoluble} = 100 (\text{g THF insoluble}/\text{g feed weight})$. Feed weight is defined as the sum of the weights of lignite (daf) and plastic mass (daf) charged to the reactor. The added catalyst was subtracted from the residue obtained.

RESULTS AND DISCUSSION

A series of thermal and catalytic coliquefaction tests was performed on waste plastics–lignite mixtures using four catalyst precursors, for example, NiN, FeN, Zr 1, and Zr 2. Several types of heavy organic solvents were also tested. The formed gaseous, hexane-soluble, and THF-soluble products were measured. Total reactant conversions were also calculated.

Figure 1 presents the conversions and product distributions obtained from waste plastics–lignite hydroliquefaction carried out thermally and over the catalysts NiN, FeN, Zr 1, and Zr 2 using a solvent petroleum residue. As indicated, the catalysts' presence enhanced considerably the reactants' conversion into gaseous and liquid products, although a variability in their liquefaction behavior was observed. It is evident that among them FeN was identified to have a slightly better performance, exhibiting considerable synergy with the reacting materials. Compared to the other series of runs, the efficacy of the conversion

Table IV Composition of the Oils Obtained from the Last Series of Experiments (wt % of Oils)

	Paraffins	Aromatics	Polar Composition
1. FeN with solvent petroleum residue	24.7	53.6	21.7
2. FeN with solvent coal-derived liquid	26.0	49.2	24.8
3. Zr 1 with solvent plastics pyrolysis oil	38.6	41.8	19.6
4. NiN with solvent tire pyrolysis oil	35.1	43.5	21.4

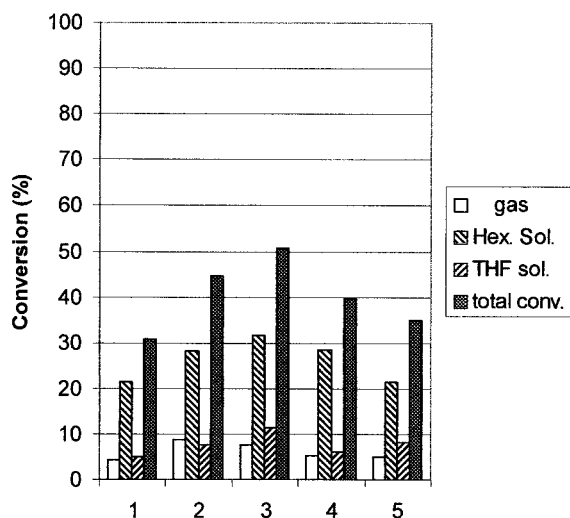


Figure 1 Waste plastics–lignite coliquefaction with solvent petroleum residue: (1) no catalyst added; (2) NiN; (3) FeN; (4) Zr 1; (5) Zr 2.

process was generally increased, as is particularly noticeable, and, indeed, in one case, total conversion and hexane-soluble products reached their highest values of 50.6 and 31.7%, respectively (Fig. 1). It is also apparent that petroleum-derived liquids proved to be the best-performing solvents, interacting as effective parameters through the multiplicity of compounds contained.

The data generated from the similar coprocessing experiments of waste polymers–lignite performed with solvent coal residue this time are summarized in Figure 2. As expected, this solvent also demonstrated favorable behavior in coprocessing, enabling the yield improvement observed in Figure 2. It should be mentioned that the presence of coal-derived polynuclear hydrocarbons combined with catalyst precursors stimulated again the reacting materials' transformation into gaseous and liquid products. This series of experiments revealed also that, under the conditions examined, the amount of solids conversion and formation of hexane-soluble substances reached their maximum values of 46.5 and 28.0%, respectively, when FeN was present.

Figure 3 illustrates the results of waste plastics–lignite coliquefaction tests carried out in the prescribed way thermally and catalytically, employing the third solvent, for example, plastics pyrolysis oil. Under the conditions examined in this series of studies, the plastics pyrolysis oil exhibited limited solvolytic effects and was con-

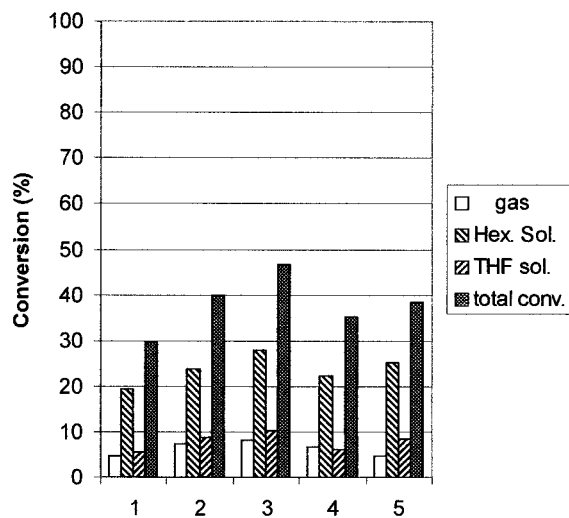


Figure 2 Waste plastics–lignite coliquefaction with solvent coal-derived liquid: (1) no catalyst added; (2) NiN; (3) FeN; (4) Zr 1; (5) Zr 2.

sidered as a rather inert solvent. Zr 1 was evaluated as the most active catalyst precursor since total conversion reached the value of 38.2%, while hexane-soluble substances were 25.7% (Fig. 3). In addition, the data collected indicated that the amount of solids conversion achieved reflected a significant distinction in the reactivity of the used solvent with NiN and FeN since their synergy appeared to be detrimental, yielding lower conversion values than that of the thermal reaction.

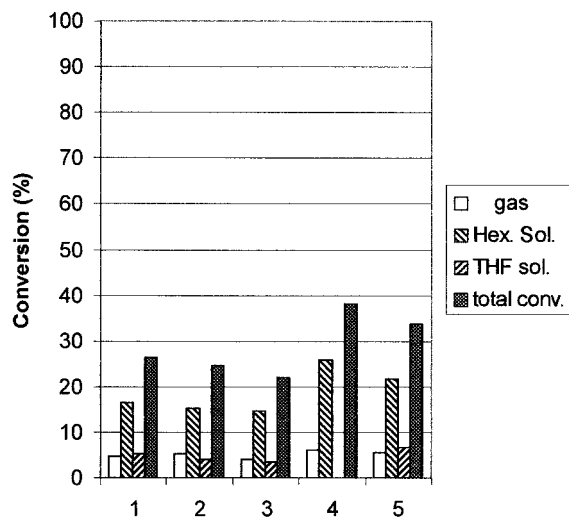


Figure 3 Waste plastics–lignite coliquefaction with solvent plastics pyrolysis oil: (1) no catalyst added; (2) NiN; (3) FeN; (4) Zr 1; (5) Zr 2.

Thermal and catalytic coliquefaction experiments were also conducted in a similar manner, employing the fourth solvent, for example, tire pyrolysis oil. The results obtained confirmed the expectation that this last solvent should demonstrate satisfactory effectiveness in coprocessing, enabling a significant breakdown of the lignitic matrix leading to the yields observed in Figure 4. It was clearly shown for this set of reactions that NiN proved to be the most active catalyst employed, followed by FeN. From the coliquefaction reactions displayed in Figure 4, the primary results obtained were at a level of 44.3 and 26.4% for total conversion and hexane-soluble products, respectively.

Based on the results obtained from the preceding investigation, another series of tests was attempted, repeating the best-performing experiment of each of the previous sets and employing, this time, pretreated lignite in order to alter the overall solids conversion attained so far. Figure 5 presents the data generated from these experiments. It is apparent that feeding the reaction with a beneficial lignite matrix enabled a large improvement in activity, promoting total conversion to show primary results to a level of 73.4% while the hexane-soluble products tracked yielded 41.6%. FeN used in conjunction with petroleum residue was found to display the best results achieved, indicating a particularly noticeable activity increase (Fig. 5).

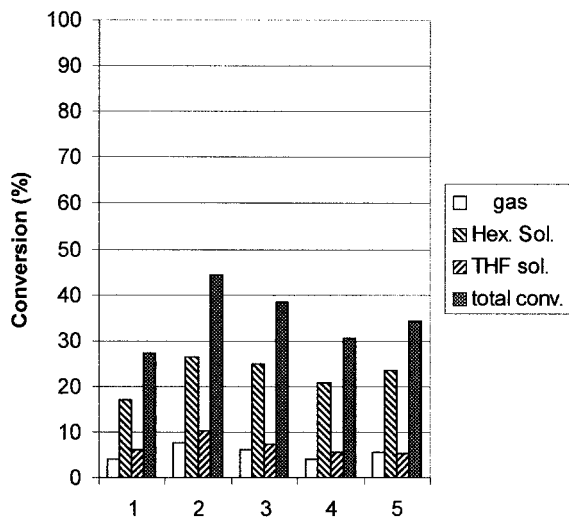


Figure 4 Waste plastics–lignite coliquefaction with solvent tire pyrolysis oil: (1) no catalyst added; (2) NiN; (3) FeN; (4) Zr 1; (5) Zr 2.

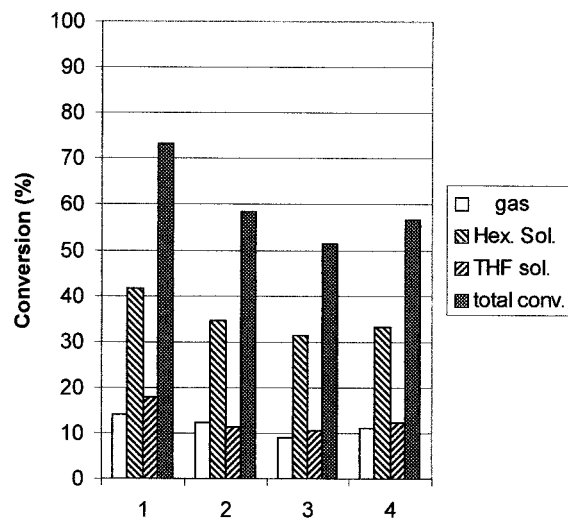


Figure 5 Waste plastics–pretreated lignite coliquefaction: (1) FeN with solvent petroleum residue; (2) FeN with solvent coal-derived liquid; (3) Zr 1 with solvent plastics pyrolysis oil; (4) NiN with solvent tire pyrolysis oil.

Even better results were obtained when two-successive-stage processing was performed. This study was undertaken to investigate whether liquefied plastics can be used as a solvent media for lignite, optimizing, thus, the product distribution of this highly complex transformation. In the first stage, the plastic feedstocks were initially liquefied with different solvents over the corresponding most active catalyst precursors. Then, pretreated lignite matrix was added in the formed oily products and the second stage of coliquefaction followed. The conversion and product distribution determined are shown plotted in Figure 6, displaying an additional yield improvement from this last hydroliquefaction series. It is evident that pretreated lignite matrix free of the majority of ashes had the propensity to be an effective reaction parameter, affecting, positively, two-stage processing. Total conversion and hexane-soluble products reached their highest values of 82.5 and 46.8%, respectively, when FeN in conjunction with the petroleum residue catalyzed the reaction.

Finally, the composition of the gases and oils obtained from the last series of experiments was determined (Tables III and IV), demonstrating similarities and differences among the products yielded. The main trend observed in the gaseous products is that they favored the formation of unsaturated hydrocarbons and oxygenated mole-

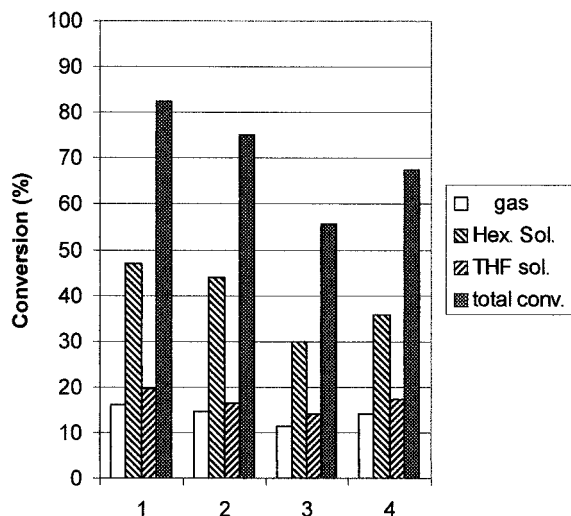


Figure 6 Waste plastics–pretreated lignite coliquefaction in two stages: (1) FeN with solvent petroleum residue; (2) FeN with solvent coal-derived liquid; (3) Zr 1 with solvent plastics pyrolysis oil; (4) NiN with solvent tire pyrolysis oil.

cules which were considered to be a result of an extended reacting substances' catalytic cracking. In the oily phase, it was detected that polar compounds consisted of a minority regardless of the used catalysts' character, while as a majority accounted for the desired aromatics. It is noteworthy that this last observation is in good agreement with previous studies²⁶ postulating that aromatic compounds act like a hydrogen shuttle for the stabilization of the formed radicals and a sufficient percentage of these substances is needed in order for the hydrogenation to proceed successfully, avoiding retrogressive reactions for coke formation.

CONCLUSIONS

Based on the results obtained of the presented studies, it is concluded that catalytic coprocessing of waste plastics mixtures with lignite may become a promising way of hydrocarbon synthesis. Under the conditions examined, it was found that the efficacy of the conversion displayed was dependent on the synergy of the solvents and catalysts employed and that catalyst addition increased, in general, the yield formation. It was also found that catalytic reactions using petroleum residue and coal-derived liquids displayed

adequate solvolytic effects for the reacting solids. On the contrary, tire pyrolysis oil and plastics pyrolysis oil did not interact readily at coliquefaction conditions.

The study demonstrated, furthermore, that oxidatively pretreated lignite proved more effective than did the raw material in promoting sufficiently coliquefaction product yields. In the corresponding experiments, the highest activity was displayed by a mixture of pretreated lignite, waste plastics, FeN, and petroleum residue.

Finally, the two-successive-stage experiments conducted achieved the desired optimization of the process. The synergism observed due to the combined effect of the method increased hydroliquefaction yields to a level of 82.5% for total conversion and 46.8% for hexane-soluble products when in a reaction mixture of waste plastics, petroleum residue, and FeN pretreated lignite was added.

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