

NON-HYDROGENATING AND HYDROGENATING SUPERCRITICAL EXTRACTION OF TURKISH COALS

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In this study, the effect of molecular hydrogen and hydrogen donor during the extraction of two different coals with toluene was investigated employing the non-isothermal semi-continuous technique. The experiments were carried out to investigate the effect of source of hydrogenating agent on conversion degree and extract yield. The results clearly indicate that the hydrogenating affect of hydrogen donor solvent is stronger than molecular hydrogen and the use of molecular hydrogen in supercritical coal extraction processes not always improves coal conversion and extract yields.

INTRODUCTION

It is known that the extraction of bituminous coal and lignite with sub- and supercritical solvents have shown the limited conversion degree and the extraction yield up to 30-40 % . The optimizing of process parameters cannot improve these yields significantly. Additional hydrogenation of coal during extraction process seems to be needed to increase the yield of liquid hydrocarbon and conversion degrees. In the hydrogenating extraction process, coal reacts at elevated temperatures and pressures with a mixture of conventional solvent such as toluene and gaseous hydrogen and/or a hydrogen donor solvent and optionally a catalyst. The

aim of the addition of hydrogen is to increase the H/C ratio in the extraction products and to avoid the further aromatization during the carbon-carbon bond formation that increases molecular size and loss of hydrogen. According to the conditions used, distillate fuel oils, chemical feedstock and high molecular weight hydrocarbons can be obtained.

Indigenous primary energy sources of Turkey include lignite, bituminous coal, geothermal, wood, animal and plant wastes, solar and wind. Lignite is the dominant energy source produced in Turkey. The primary energy reserves of in Turkey are lignite 8375 million tons, bituminous coal 1126 million tons, asphaltite 82 million tons, bituminous schist 1641 million tons, oil 49 million tons, hydropower 35045 MW/year and geothermal 35600 MW/year [1]. The consumption of major energy source, lignite, is approximately 50 million tons in a year. All projections into future, like growth of population and enhanced industrialization/living standards, expects the feasible using of its primary energy sources. The growing of energy demand and chemical raw material in Turkey needs to optimize the using its own resources such as lignite. Nearly 75 % of indigenous lignite is consumed in thermal power plants.

The present study is undertaken to investigate extraction of some Turkish coals and ascertaining liquefaction yields and liquefaction rates as a function of given extraction conditions. In this paper it was presented some experimental findings which show that hydrogenating extraction can affect the conversion degree and liquid hydrocarbon yield in certain circumstances.

MATERIALS AND METHODS

The details of analysis of chosen coal samples (Ermenek lignite and Zonguldak bituminous coal) are given in Table 1. Samples were crushed and sieved to obtain a 0.3-1 mm fraction for the extraction experiments.

Application of liquid and supercritical extraction of turkish coals (bituminous coal and lignite) were investigated using a non-isothermal experimental technique. Figure 1 shows schematically the apparatus used for this investigation. A fixed bed of coal particles was

slowly heated (heating rate of 5 K/min) in a current of pressurized toluene (10 MPa) and mixture of toluene and hydrogenating agent.

Table 1. Results of the analysis of coal samples

	Ermenek lignite	Zonguldak bituminous coal
Proximate analysis (wt %)		
Moisture	14.5	2.2
Volatile matter	44.5	24.0
Ash	21	13.0
Elemental analysis (wt %)		
C	73.6	85.4
H	4.9	4.5
N	0.5	1.1
S	1.2	0.6
O (from diff)	19.8	8.4

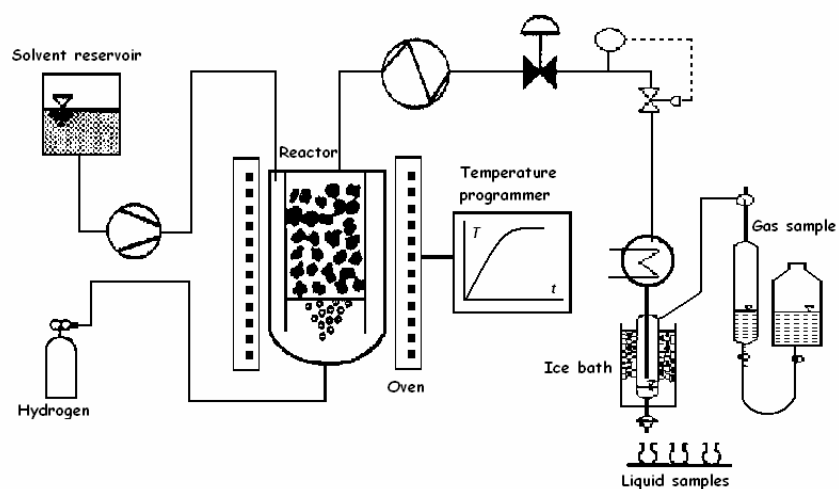


Figure 1. Experimental apparatus for non-isothermal coal hydrogenation

During the extraction solvent changes its physical state from a liquid to supercritical fluid. With the help of the technique used, it was possible to obtain information about integral yields and also extract formation rates in the entire temperature range. The effluent containing the extract as well as liquid and gaseous coal decomposition products were analyzed in short time intervals at rising temperature. Extract formation rates were continuously measured from ambient temperature (25 °C) to the end temperature (550 °C). The extract formation rate profiles over the temperature show differences depending on the combination of solvent and hydrogenating agent which is used as an extracting fluid. The effect of the addition of molecular hydrogen and hydrogen-donor solvent (tetralin) to supercritical phase with and without catalyst was also studied

RESULTS

The final degree of coal conversion and the yield of dissolved extract change through the addition of gaseous hydrogen to liquid toluene are shown in Figure 2. Conversion degree for bituminous coal and lignite with toluene extraction were 30 wt % and 28 wt %, respectively. The addition of hydrogen increases the coal conversion with increasing molar ratio H₂/toluene. Firstly, the extract yield increases with increasing the amount of added hydrogen, reaches a maximum value, than decreases at the higher hydrogen molar ratio. Two parameters can play an active role in the degradation of the coal structure during hydrogenating extraction. Firstly, hydrogen transfers occur from extraction medium to radicals to form stable compounds [2]. The further increasing of the gaseous hydrogen can causes the density reduction, which leads to decrease the amount of extracted compounds.

The conversion degree increases for both bituminous coal and lignite with increasing the H₂/solvent mole ratio. The increase for lignite is greater than for bituminous coal because of the sensitivity of oxygen rich structure of lignite. Enhanced hydrogenation of the lignite's oxygen rich structure leads to the more extractable material with increasing mole ratio and overwhelm the density reduction of the fluid phase caused by the addition of a dilute gas (H₂). In the coal hydro-liquefaction process, another way to obtain valuable compounds is pyrolysis

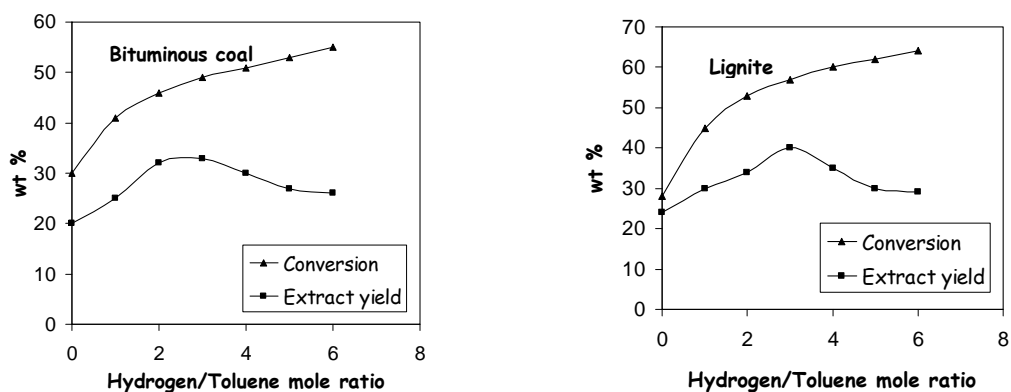


Figure 2. Effect of the addition of gaseous hydrogen on coal conversion and extract yield for bituminous coal and lignite

of coal at elevated temperatures in the presence of a hydrogen donor solvents such as tetralin, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, and 4,5-dihydropyrene. In this study, tetralin is used to provide a transport medium for the products as well as a convenient liquid source of hydrogen for the degradation. The addition of hydrogen donor solvent strongly increases extract formation rate and coal conversion. The addition of 10 wt % tetralin to toluene during supercritical extraction gives 40 wt % and 15 wt % increase in conversion degree for lignite and bituminous coal, respectively. The increase of extract yields of lignite and bituminous coal were 16 wt % and 12 wt %, respectively. The generated reactive free radicals abstract hydrogen from donor solvent, thereby forming stable compounds. It can be seen that tetralin is a stronger liquefaction solvent than gaseous hydrogen. Sangon et al have been founded that the for tetralin addition (10-70 %) to toluene, coal liquid yield increased with tetralin content up to 30 % [3]. Thus, tetralin content of about 30 vol % may be sufficient to inhibit the recombination of radicals. Under near and supercritical conditions molecular hydrogen – even if activated with a catalyst – is much less efficient as a hydrogenating agent

than a donor solvent. When catalyst was added to the coal no influence to lighter products during the extraction with toluene-tetralin mixtures can be seen. The catalyst (tin chloride) improves conversion and extract yields, when molecular hydrogen is used with non-donor solvent toluene. When the mixture of toluene and tetralin was used as solvent and molecular hydrogen was added to this mixture, conversion degree and extract yield decrease with increasing H₂/solvent mole ratio for both coal samples (decreasing of extract for bituminous coal and lignite are 13 % and 9 %, respectively). The possible reason is the reduction of extract solubility in the supercritical fluid due to its dilution with gaseous hydrogen.

CONCLUSION

The role of supercritical toluene extraction and the effects of hydrogen donor solvent and gaseous hydrogen are investigated. Supercritical toluene is effective for the extraction of bituminous coal and lignite at high pressure and temperature. Hydrogen donor solvent such as tetralin is required for suppressing the aromatization of coal. The results indicated that the addition of donor solvent to the toluene is effective than the addition of molecular gaseous hydrogen at the same extraction conditions. Fluid density also plays an important role in extraction of coal in toluene-gaseous hydrogen mixtures. Up to 55 % liquid yield can be achieved in extraction with toluene-tetralin mixture using a semi-continuous reactor.

The experimental results show, that the use of molecular hydrogen in supercritical coal extraction processes not always improves coal conversion and extract yields.

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