

Article

Recycling Molybdenum from Direct Coal Liquefaction Residue: A New Approach to Enhance Recycling Efficiency

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Received: 4 February 2020; Accepted: 5 March 2020; Published: 6 March 2020



Abstract: In this paper, direct coal liquefaction residue was prepared from Shen-dong coal, and the solubility of the residue in five organic solvents was studied. Then, an experimental device was set up to recover molybdenum (Mo) compounds from the direct coal liquefaction residue after extraction, and the influences of sublimation temperature and duration on recycling efficiency were examined. The recycled Mo-based products were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), and a thermal analyzer. The results reveal that the optimum extraction conditions were obtained through ultrasonic extraction with a quinoline solvent and the highest recycling efficiency occurred for sublimation at 900 °C for 30 min. The recycled products are identified to be α -MoO₃ crystals. Moreover, the α -MoO₃ crystal is thermally stable before the temperature reaches its melting point.

Keywords: direct coal liquefaction residue; molybdenum recycling; sublimation and condensation; α -MoO₃ crystal

1. Introduction

Direct coal liquefaction is an important technique, which contributes to the efficient conversion and clean utilization of raw coal [1–3]. It is a powerful way to transform raw coal to liquid oils when high temperatures and pressures are applied, in the presence of hydrogen gas and catalysts. Catalysts play a vital role in the transforming process, since they can lower the cost of oil products and make the transformation much easier [4].

Widely used, efficient catalysts for the direct coal liquefaction reaction include Iron (Fe)- and Molybdenum (Mo)-based materials and some metallic composites [5–8]. Fe-based catalysts are economical and are quite active to hydrogenate olefins and free radicals. Iron ore (61.5%–63.5% Fe) as a raw material for catalyst preparation is cheaper than molybdenite by \$140 per ton [9]. However, they only have moderate catalytic activity to break bonds in aromatic rings, methylene bridges, and alkanes, in addition to dislodging heteroatoms, such as S (Sulfur), N (Nitrogen), and O (Oxygen). Mo-based catalysts have high catalytic activities for both hydrogenation and heteroatom purification, leading to a high efficiency of coal transformation. However, Mo-based catalysts have such high material costs that it is necessary to recycle Mo from the direct coal liquefaction residue (DCLR) for reuse.

DCLR is a byproduct of direct coal liquefaction [10]. In the liquefaction process, coal is hydrogenated to form gases, water, and liquid oils, which have a broad range of fractions. The heavy fraction and solid residues in the coal slurry include catalysts, ashes, and unreacted coal that can be separated in a depressurized distillation tower. Afterwards, part of the heavy oil and asphalt-based materials (asphaltene and preasphaltene) and all other solid residues are eliminated from the tower. They become DCLR after being cooled down and solidified.

The DCLR constitutes about 30% of the raw coal [11,12], and 30% of the DCLR is unreacted coal that does not dissolve in organic solvents, such as tetrahydrofuran, and thus the unreacted coal can be separated easily. Moreover, 20% of the DCLR is inorganic compounds, which are composed of the original mineral substances from the raw coal, newly generated mineral substances, and the metallic catalysts [13,14]. In fact, the compositions of coal, including exinite, vitrinite, and inertinite, have been confirmed by high-resolution microscopes. Micrographs showed that the exinite and vitrinite were totally transformed and inertinite was partly transformed into low molecular weight liquid fuels by direct coal liquefaction [15]. As a result, the unreacted inertinite could also be imaged by microscopes, in addition to the mesophase microbeads and semi-coke.

Since Mo-based catalysts mix together with the other solids in the DCLR, it is quite difficult to directly recycle Mo compounds and achieve a cyclic utilization. Approaches to recycle Mo from DCLR have recently been developed and the most promising one is wet alkaline extraction. In this method, the Mo containing DCLR is first placed in an alkaline solution and the resulting solution is then concentrated and crystallized. As a result, a small amount of Mo is obtained. Xie et al. [16] developed this method and they first calcined the mixture of DCLR and a solid alkali and then placed the baked mixture in water. After concentration and crystallization, they successfully obtained molybdate from the solution. Sebenik et al. [17] invented a method to transform molybdate into a Mo-based catalyst. They placed the DCLR in an alkaline solution to dissolve the molybdate and form a Mo alkali compound simultaneously. Subsequently, they baked the Mo alkali compound in oxygen at 600–800 °C for 1 h. The resulting oxide was then acidified and ammoniated in order to form a Mo-containing precipitate. The Mo deposits were further ammoniated to produce Mo-based catalysts for future use. Ference et al. [18] studied Mo recycling and reuse in two different DCLR systems with Mo-based catalysts. They mixed Na₂CO₃ (sodium carbonate) powder with the two DCLR, baked the mixture, and immersed it in 100 °C water, before adding Ca(OH)₂ (calcium hydroxide) or CaCl₂ (calcium chloride) to form CaMoO₄ (calcium molybdate) deposits. Finally, the Mo was recycled by filtering, washing, and drying the CaMoO₄ deposits. Song et al. [19] studied the process of recycling vanadium, molybdenum, and uranium at the same time from high calcium coal residue. They conducted the following processes in order to eventually separate the three elements: raw coal-decarburization by baking; decalcification in sulfuric acid; sodium salt roasting; cyclic immersion; salt-out the vanadium precipitate; and uranium extraction in acid. Overall, though the wet alkaline extraction and other traditional methods, such as selective chlorination, acid-leaching, and electrolysis processes [20–22], are useful to recycle Mo from a small amount of DCLR, the recycling efficiency of Mo element has always been low. In fact, it can be fairly time and water consuming if a large amount of DCLR, which constitutes about 30% of the raw coal, needs to be recycled in industrial applications.

Mo oxide has a melting point of 795 °C and it sublimates easily at the temperature above 600 °C. If Mo compounds from DCLR are heated at 800–1000 °C in oxygen, the (MoO₃)₃ forms and condenses after cooling down [23–27]. This fact inspired us to develop a method to increase the recycling efficiency of Mo element from DCLR using first a high temperature sublimation and then a low temperature condensation process. We also investigated the influences of sublimation temperature and duration on the recycling efficiency, characterized the recycled Mo oxide, and revealed its thermal stability.

2. Results and Discussion

2.1. Solubility of the Original DCLR

Figure 1 shows the solubility of the original DCLR in the five organic solvents. The original DCLR had the lowest solubility in normal hexane (3.38%) and the highest solubility in quinoline (61.26%), indicating that the quinoline was the most appropriate solvent for the degradation of the original DCLR.

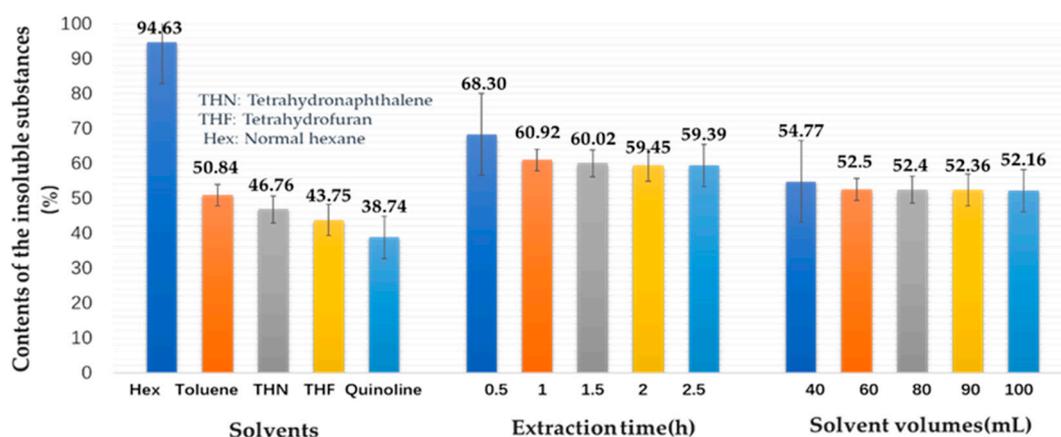


Figure 1. Solubility of the original direct coal liquefaction residue (DCLR) in different organic solvents for different extraction durations and different solvent volumes.

Moreover, the influence of ultrasonication duration on the solubility of the original DCLR in tetrahydrofuran is shown in Figure 1. Increasing the ultrasonic duration from 0.5 to 1 h led to an increase in solubility from 31.97 to 39.08%. However, the solubility did not benefit from further increases in the ultrasonication duration.

The volume of extraction solvents had a minor effect on the solubility of the original DCLR, as shown in Figure 1. When 40 mL of solvent was added to 10 g of the original DCLR, the solubility was 45.23%. This value increased slightly to 47.50% when 60 mL solvent was used, but additional solvent did not further increase the solubility.

2.2. Recycling Efficiency of Mo-Based Catalysts

Table 1 shows the compositions of the original DCLR and the residual DCLR after recycling. The content of the sample (oxides of molybdenum, iron, aluminum, calcium, silicon, and sulfur) was measured using a Panalytical Axios 4400/40 X-ray fluorescence spectrometer (XRF) (Netherlands). Table 1 shows that the composition of the DCLR changed greatly after recycling and the SO_3 content decreased from 44.79% to 0%, indicating that the reaction process at high temperatures efficiently degraded the metal sulfides.

Table 1. Composition of the original DCLR and the residues after recycling.

Measuring conditions	Line Crystal	MoO_3	Fe_2O_3	Al_2O_3	CaO	SiO_2	SO_3
		k_α LiF200	L_α LiF200	k_α LiF200	k_α LiF200	k_α PE002	k_α LiF200
Content of each component (%)	Original DCLR	49.93	0.17	3.63	0.03	0.06	44.79
	Residues after recycling	65.60	10.70	2.68	8.19	7.25	0.00

The recycling efficiency of the Mo-based catalyst was dependent on the sublimation temperature, duration, and the Mo concentration of the original DCLR. The influences of temperature and

duration on the recycling efficiency were evaluated using pure MoS₂ (Molybdenum sulfide) in the sublimation-condensation process. Then, at the optimized temperature and duration, the recycling efficiency of the Mo-based catalysts from the original DCLR, which had different Mo concentrations, was determined.

2.2.1. Sublimation Temperature

The recycling efficiency of Mo-based catalysts was shown in Figure 2 with the increase in sublimation temperature from 750 to 950 °C, for the same duration of 30 min. The efficiency was relatively low at 750 °C (25%), but it increased by more than three times when the temperature reached 800 °C. Further increases in temperature only resulted in slight increases in the efficiency. The highest efficiency was 99.6% at 900 and 950 °C, indicating that 900 °C was sufficient for recycling Mo-based catalysts. Overall, the optimized sublimation temperature was between 800 and 900 °C.

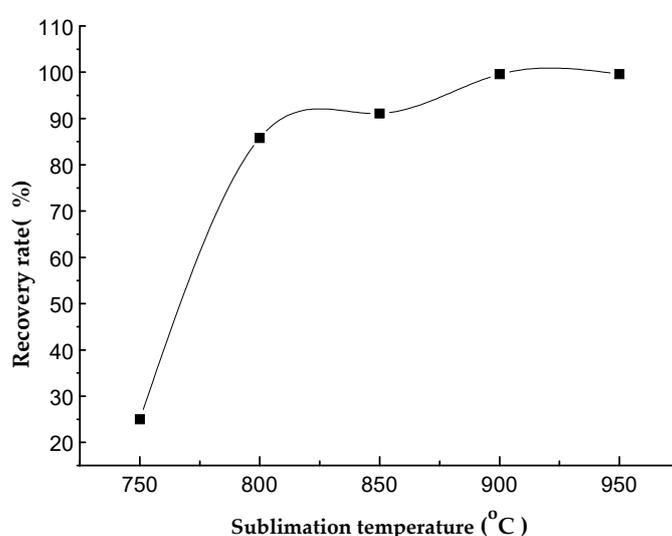


Figure 2. Recycling efficiency of Mo-based catalysts with an increasing sublimation temperature.

2.2.2. Sublimation Duration

The sublimation duration had a minor effect on the recycling efficiency of Mo-based catalysts, as shown in Table 2. When the sublimation process lasted for 15 min, the efficiency was about 78.1%. Efficiency reached 99.6% when the sublimation duration was 30 min or longer. Clearly, the optimized duration of sublimation at 900 °C was 30 min.

Table 2. Recycling efficiency of the Mo-based catalysts for different sublimation durations.

Sublimation Temperature (°C)	Condensation Temperature (°C)	Sublimation Duration (min)	Recycling Efficiency (%)
900	400	60	99.6
900	400	45	99.6
900	400	30	99.6
900	400	15	78.1

2.2.3. Mo Concentration in the Residue DCLR after Extraction

Previous results showed that the optimized sublimation temperature and duration were 900 °C and 30 min for pure MoS₂. The residual DCLR after extraction had different Mo concentrations, similar to the pure MoS₂ material, and thus the recycling efficiency also differed correspondingly. Table 3 shows the recycling efficiency of Mo-based catalysts from the residue DCLR after extraction with

different Mo concentrations from 40% to 60%. The recycling efficiency experienced a rapid increase from 40.5% to 99.5% with an increase in Mo concentration from 40% to 60%.

Table 3. Effect of the content of Mo in the residue DCLR after extraction on recycling efficiency.

Contents of Mo in the DCLR Materials after Reaction (%)	Recycling Efficiency (%)
40	40.5
50	78.5
55	87.6
60	99.5

Overall, both the sublimation temperature and the duration had remarkable effects on the recycling efficiency of the Mo-based catalysts. The sublimation temperature of 900 °C, condensation temperature of 400 °C, and the 30 min duration were optimal for recycling Mo-based catalysts. Moreover, the recycling efficiency of the Mo-based catalysts was also affected by the Mo concentration in the residual DCLR after extraction. A larger concentration of the residual Mo meant higher efficiencies, suggesting that it was necessary to increase the sublimation temperature and duration in order to increase the recycling efficiency of low Mo containing residual DCLR after extraction.

2.3. Characterization of the Recycled Mo-Based Products

2.3.1. Microstructure Analysis

The microscopic morphologies of the samples that were recovered at different condensation temperatures were observed, as shown in Figure 3. Multilayered tabular crystals formed the products at 25 and 200 °C, whereas irregularly distributed strip crystals developed at the higher condensation temperature of 400 °C, and the crystal size was smaller than that of the recovered sample with a low sublimation temperature, as shown in Figure 3c. This is mainly due to the rapid growth and aggregation of crystals caused by the accelerated rate of sample condensation at lower temperatures.

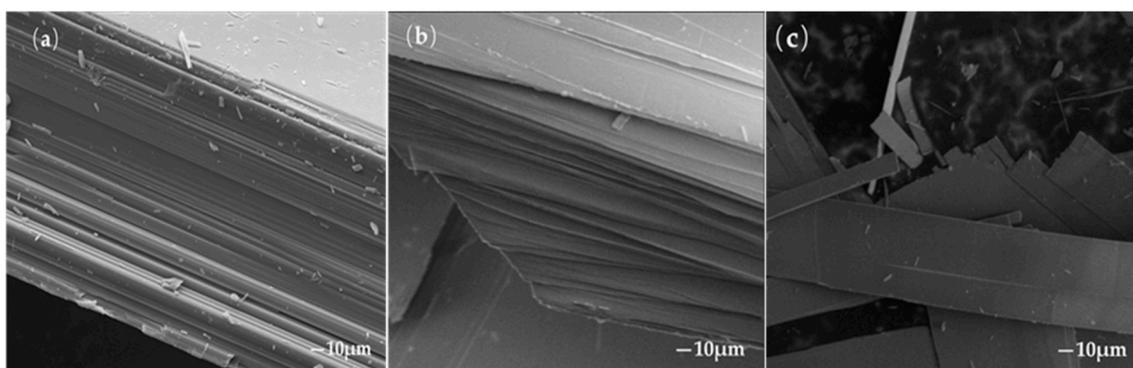


Figure 3. Scanning electron microscopy (SEM) images of the recycled Mo-based products at different condensation temperatures (a) 25 °C, (b) 200 °C, (c) 400 °C.

X-ray diffraction (XRD) analysis was performed on the products at a condensation temperature of 200 °C to reveal the phases of the products. The XRD spectrum is shown in Figure 4. The XRD peaks were consistent with the standard peaks of MoO₃. The strong peaks at $2\theta = 12.6^\circ$, 25.8° , and 39.0° were clearly observed and they correspond to the (020), (040), and (060) crystallographic planes of MoO₃, respectively. Moreover, two weak peaks were observed at $2\theta = 23.6^\circ$ and 27.4° , corresponding to the (110) and (021) planes. The crystal lattice constants (a, b, c) were also analyzed and the results are listed in Table 4. Two samples were analyzed by XRD and the results agreed well with each other and were consistent with the data from [27]. The data in Table 4 indicated that the lattice constants varied ($a = c \neq b$), but the crystallographic angles were the same ($\alpha = \beta = \gamma = 90^\circ$). Thus,

the above results classified the phase of the products as α - MoO_3 , belonging to a stable orthorhombic crystallographic system.

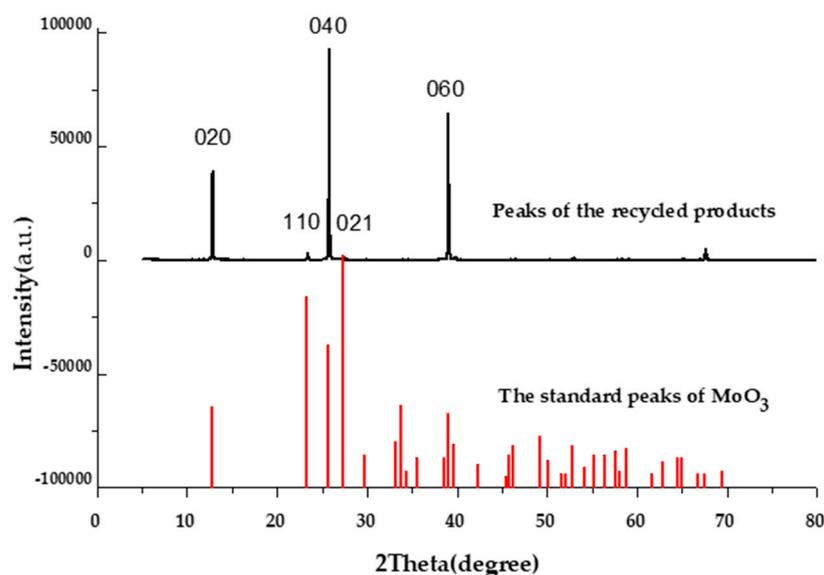


Figure 4. X-ray diffraction (XRD) peaks of the recycled products and the standard pattern peaks of MoO_3 .

Table 4. Crystal lattice constants of the recycled and α - MoO_3 .

Samples	a/ 10^{-1} nm	b/ 10^{-1} nm	c/ 10^{-1} nm
1	3.957	13.841	3.693
2	3.960	13.848	3.694
α - MoO_3	3.962	13.858	3.697

Figure 5 shows the Fourier-transform infrared spectroscopy (FT-IR) spectrum of the products at a condensation temperature of 200 °C. A broad adsorption peak range could be observed between 400 and 1000 cm^{-1} . Specifically, the noticeable adsorption peaks were at 475 cm^{-1} , 547 cm^{-1} , 816 cm^{-1} , 839 cm^{-1} , and 995 cm^{-1} , respectively. These results can be attributed to the stable crystallographic structure of α - MoO_3 . In the structure of α - MoO_3 , each Mo atom is surrounded by distorted $[\text{MoO}_6]$ octahedrons, which share crystal edges and the equatorial apex angle [26,28]. In each $[\text{MoO}_6]$ octahedron, a single oxygen atom ($\text{Mo}=\text{O}_{(1)}$) occupies the lattice endpoint and two axial oxygen atoms ($\text{Mo}-\text{O}_{(2)}$) share two octahedra, and, at the same time, three equatorial oxygen atoms ($\text{Mo}-\text{O}_{(3)}$) share three octahedra. The three types of oxygen atoms represent three modes of stretching vibrations between Mo and O, which can be observed by FT-IR. Thus, in the spectrum in Figure 5, the energy of the stretching vibration of the typical $\text{Mo}=\text{O}_{(1)}$ double bond was adsorbed by the compound, which corresponds to 995 cm^{-1} . Meanwhile, the stretching vibrations of the $\text{Mo}-\text{O}_{(2)}$ and $\text{Mo}-\text{O}_{(3)}$ single bonds corresponded to the adsorption peaks at 816, 839 cm^{-1} and 475, 547 cm^{-1} , respectively. Overall, the XRD and FT-IR results indicate that the recycled products from the DCLR were α - MoO_3 crystal.

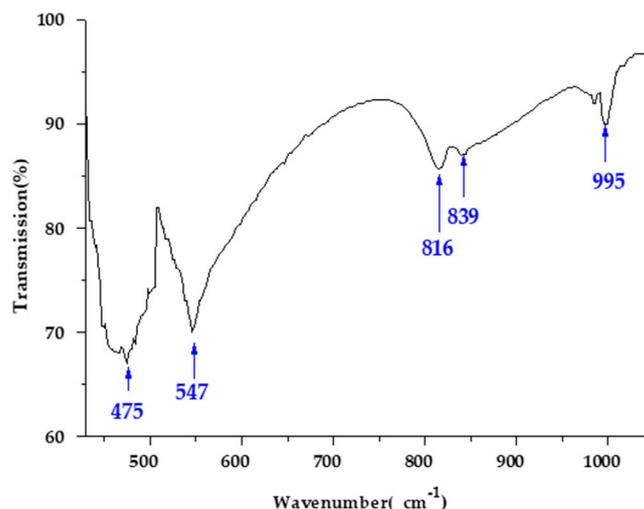


Figure 5. Fourier-transform infrared spectroscopy (FT-IR) spectrum of Mo oxide at the condensation temperature of 200 °C.

2.3.2. Thermal Stability of the Recycled Products

Figure 6 shows the temperature-dependent weight loss of the recycled products from 200 to 1050 °C. The curves had three stages with an increasing temperature. Almost no change happened during stage I from 200 to 795 °C. The weight loss of the sample was 6.2% and the heat flow was in the range between 0 and 190 mW (milli Watts). At stage II, from 795 to 885 °C, the heat flow increased sharply, resulting in a sudden loss of weight. Then, at stage III, from 885–1050 °C, weight loss was evident because the temperature was higher than the melting point of α -MoO₃ (795 °C). At the end of the three stages, the ratio of weight loss reached 97.7% at a relatively high heat flow of 190 mW (milli Watts).

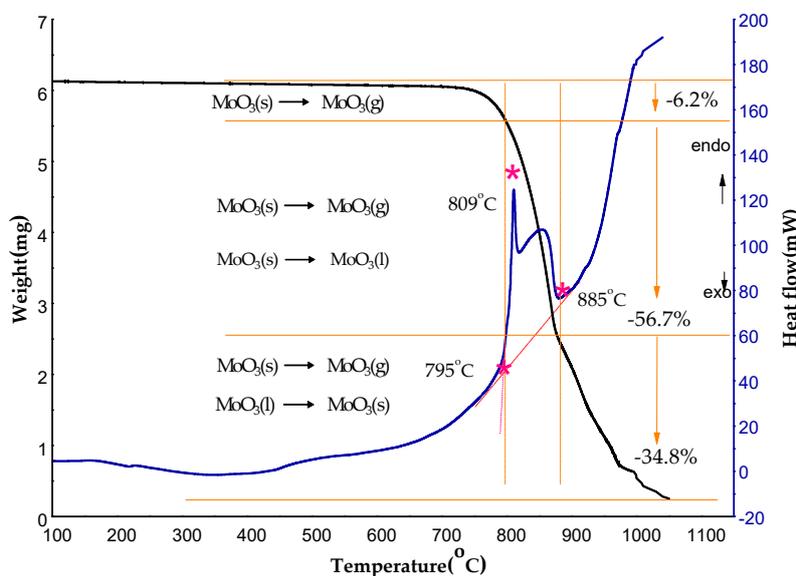


Figure 6. Thermal stability of the recycled Mo-based products.

In conclusion, the sublimation-condensation process proposed in this paper to recycle molybdenum from DCLR can overcome the disadvantages of wet methods and enhance recycling efficiency. The recycled products presented a semi-transparent structure. The phase of the lamellar products was identified to be α -MoO₃ crystals. Figure 7 shows a flow diagram with optimal parameters for molybdenum recovery from DCLR.

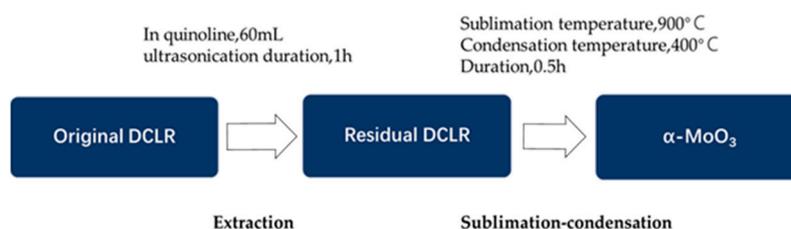


Figure 7. Flow diagram with optimal recycle parameters.

3. Materials and Methods

3.1. Reagents and Materials

Normal hexane, toluene, tetrahydrofuran, tetrahydronaphthalene, and quinoline (analytical grade) were purchased from Sino pharm (Jiangsu, China). Molybdenum sulfide (99.5% metals basis) was purchased from Aladdin® (Shanghai, China). Coal was obtained from China Energy Shen-dong Coal Group (Ordos, China). Table 5 shows the quality of Shen-dong coal.

Table 5. The results of Shen-dong coal quality analysis.

Industrial Analysis (%)			Elemental Analysis (%)					Petrographic Analysis (%)				
M _{ad}	A _d	V _{daf}	FC _d	C _d	H _d	N _d	S _d	O _d	Vitrinite	Inertinite	Exinite	Minerals
4.72	7.62	37.73	57.53	74.15	4.97	0.99	0.26	12.01	54.6	41.7	1.2	2.5

M_{ad}, A_d, V_{daf}, FC_d are Air-drying moisture, Dry-based Ash, Dry ash-less volatile and Dry-based carbon; C_d, H_d, N_d, S_d, O_d are Dry-based Carbon, hydrogen, nitrogen, sulfur, and oxygen.

The quality of raw coal is the key factor in determining the efficiency of direct coal liquefaction [29,30]. The younger the coal, the more volatile it is and the easier it is to liquefy. In addition, the higher the hydrogen/carbon (H/C) atomic ratio, the less hydrogen is consumed during liquefaction. In the process of direct coal liquefaction, the coal with volatiles greater than 35%, ash less than 10% and a H/C ratio greater than 0.8 is usually selected. As shown in Table 5, the H/C ratio of Shen-dong coal is 0.80, the volatile is 37.73%, the ash is 7.62%, and the active component is 55.8%. The quality of raw coal conforms to the standard of direct coal liquefaction with high conversion.

3.2. Preparation of the Original DCLR

Shen-dong coal was used as the raw material to prepare the original DCLR by the direct coal liquefaction technology. Three steps were required to produce the original DCLR, as shown in Figure 8. The first step was to mix raw coal, a Fe–Mo-based catalyst, and hydrogen donor solvent in a coal slurry kneader for about 1 min to produce a homogeneous coal slurry. Afterwards, the mixture was pressurized in a charge pump and then heated in a coal slurry furnace under hydrogen. The heated mixture was transported to a direct coal liquefaction reactor and reacted at 455 °C and 19 MPa. After the reaction, a liquid mixture was produced, which was then separated at high pressures (19 MPa) and medium pressures (3 MPa) in separation cells, resulting in gases, water, and light oils. The residual liquid mixture was successively passed through an atmospheric pressure distillation tower and a depressurized distillation tower to separate solids from the liquid. The final liquid was the universal oil products. The solids at the bottom of the depressurized distillation tower are the original DCLR and then molded for use in experiments.

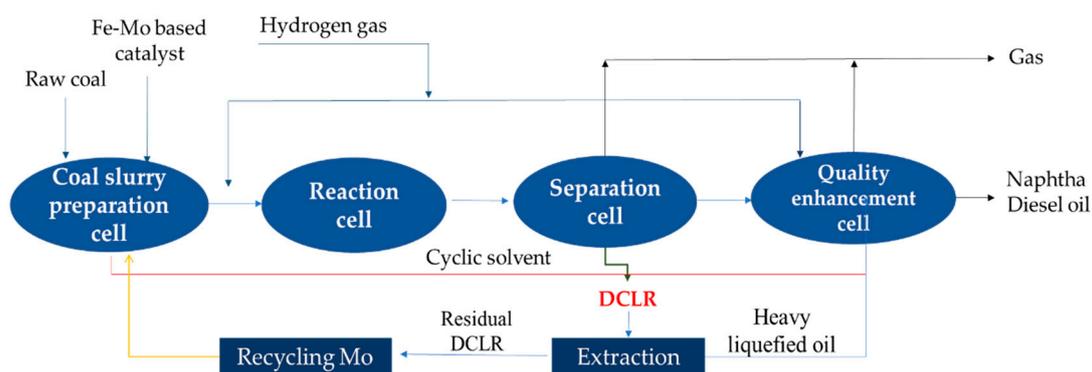


Figure 8. Processes to prepare the DCLR and recycling Mo-based product from residual DCLR.

3.3. Extraction of the Original DCLR in Organic Solvents

Half of the original DCLR is made up of heavy liquefied oils and asphalt-based materials, which could be separated with organic solvents using ultrasonic extraction technology [31]. The radiation pressure from ultrasound-induced intensive cavitation, destabilization, and acceleration of the solvent molecules to enhance their frequency and velocity, leading to a high penetration in the original DCLR. After extraction, the heavy liquefied oil could be used as cyclic solvents (Figure 8). The residual DCLR after extraction served as the raw materials to recycle Mo-based catalysts.

Five organic solvents were used in this study, including normal hexane, toluene, tetrahydrofuran, tetrahydronaphthalene, and quinoline. The solubility of the original DCLR in these solvents was revealed to evaluate their ability to dissolve the original DCLR. The influence of the ultrasonic extraction time on the solubility of the original DCLR in tetrahydrofuran was investigated. Ten grams of depressurized DCLR was put in a beaker containing 40 mL of preheated tetrahydrofuran solution (50 °C), then the beaker was placed in a ultrasonication instrument (Elmasonic S 100H, Singen, Germany, Figure 9) for 0.5, 1, 1.5, 2, and 2.5 h. The influence of the amount of solvent on the solubility was also revealed to discover an appropriate ratio of solvent to DCLR. Ten grams of depressurized DCLR were put into beakers containing different amounts of organic solvents (40, 60, 80, 90, and 100 mL). These experiments were implemented to obtain the post-extraction residual DCLR containing the most Mo as possible.



Figure 9. The ultrasonication instrument for the extraction of the original DCLR.

3.4. Recycling Mo from the Post-Extraction Residual DCLR

Equipment was made in-house especially for recycling Mo-based catalysts, as shown in Figure 10. The recycling was a sublimation-condensation process, during which the Mo metal was separated from other metals at high temperatures and Mo oxide was condensed at low temperatures. To implement

this process, the post-extraction residual DCLR was weighed after being placed in the pre-dried quartz boat, which was then placed in the sublimation part of a quartz tube. The condensation part of the quartz tube was covered by a clean quartz socket tube, where the Mo oxide was deposited. Then, the quartz tube was heated in a furnace under oxygen. The temperature of different parts of the tube could be controlled by a computer. The temperature of the sublimation part was set between 600 and 1000 °C and the condensation part was set between 200 and 600 °C. The outlet gas was cooled down at ambient temperature before being recycled.

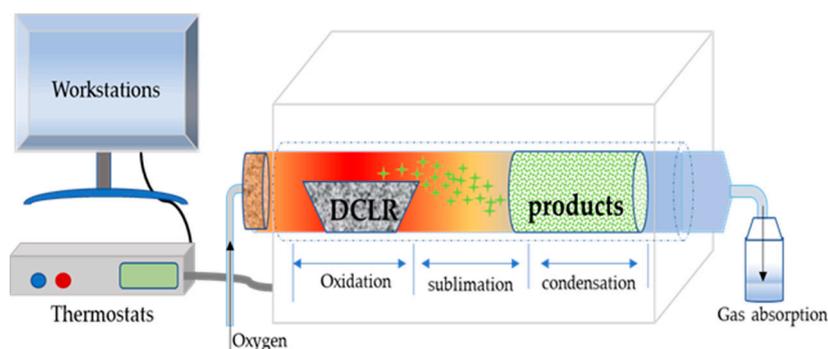


Figure 10. The schematic of the experimental set-up for recycling Mo-based catalysts.

Molybdenum sulfide was the main composition of Mo-based catalysts in the original DCLR; thus, pure MoS_2 was used in this study to better understand the influences of the sublimation temperature and duration on the recycling efficiency of Mo. The sublimation temperatures were set at 750, 800, 850, 900, and 950 °C with a 400 °C condensation temperature to evaluate the influence of the sublimation temperature on recycling efficiency. In this case, the sublimation duration at each sublimation temperature was held constant for 30 min. Then the sublimation duration was varied for 15, 30, 45, and 60 min at 900 °C to reveal the influence of the sublimation duration on the recycling efficiency. In addition, the influence of the concentration of Mo in the residual DCLR after extraction on recycling efficiency was investigated at the optimized sublimation temperature and duration.

3.5. Microstructural Observation

The recycled Mo-oxide samples were imaged by scanning electron microscopy (SEM) (FEI Nova Nano SEM 450, New York, N.Y., USA). The Mo-oxide was identified by X-ray diffraction (XRD) (Bruker D8 Advance, Karlsruhe, Germany). The scan rate of XRD was 8°/min and ranged from 10° to 100°. The Fourier-transform infrared spectroscopy (FT-IR) of the sample was measured using the IPRestige-21 FT-IR spectra-photometer (Shimadzu, Japan). The spectrum was obtained at a scanning range from 4000–400 cm^{-1} , and the number of scans was 32. The synchronous thermal analyzer (Perkin Elmer STA 6000, Waltham, M.A., USA) was used to measure the temperature-dependent weight loss of the sample as the temperature increased at a rate of 20 °C/min. The measuring range was from 200 to 1050 °C.

4. Conclusions

(1) We have analyzed the influences of organic solvent, solvent volume, and ultrasonic duration on the solubility of residue. When quinoline and normal hexane were used as solvents, the solubility difference was 57.89%. The solvent volume and extraction time have no obvious effect. The extraction efficiency was optimal after 1 hour of extraction time and 60 mL of the extraction solvent, the solubility difference between 1 hour and 2.5 hours was only 1.56%, and between 60 and 100 mL the solubility difference was 0.34%. The results show that the optimum extraction efficiency could be obtained by ultrasonic extraction in 60 mL of solvent with quinoline as the solvent for 1 h.

(2) The sublimation temperature, duration, and Mo concentration in the residue DCLR after extraction in organic solvents had great influences on the recycling efficiency of Mo. The highest efficiency was obtained at a sublimation of 900 °C and a condensation of 400 °C for 30 min. At a condensation temperature of 400 °C, a molybdenum trioxide crystal with Ultrafine banded structure can be recovered, which are smaller in size and more uniform in distribution than those with lower condensation temperatures. However, for lower Mo concentrations in the residue DCLR after extraction, a high efficiency was dependent on higher sublimation temperatures and longer sublimation times.

(3) The results in this paper are from laboratory-scale experiments and the industrial application of this method needs to be realized by more efforts to develop a large-scale recycling system.

Author Contributions: X.G. conceptualization, writing—review and editing, and supervision. C.W. methodology, the main part of the experimental and data curation, writing—original draft preparation, Y.L., K.Z., X.Y., X.Z. partial experimental and data collection. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank Yufei Zhu and Geping Shu of China Energy Investment Corporation for helpful discussions.

Conflicts of Interest: The authors declare no conflict of interest.

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