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Review

Recent Advances in Direct Coal Liquefaction

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Abstract: The growing demand for petroleum, accompanied by the declining petroleum reserves and the concerns over energy security, has intensified the interest in direct coal liquefaction (DCL), particularly in countries such as China which is rich in coal resources, but short of petroleum. In addition to a general introduction on the mechanisms and processes of DCL, this paper overviews some recent advances in DCL technology with respect to the influencing factors for DCL reactions (temperature, solvent, pressure, atmospheres, *etc.*), the effects of coal pre-treatments for DCL (swelling, thermal treatment, hydrothermal treatment, *etc.*), as well as recent development in multi-staged DCL processes, DCL catalysts and co-liquefaction of coal with biomass.

Keywords: direct coal liquefaction (DCL); processes; influencing factors; coal pre-treatment; catalysts; co-liquefaction; biomass

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1. Introduction

Due to the rapid increase in demand for petroleum and its declining reserves, the concern over energy security has intensified the interest in coal liquefaction, especially for those countries which are short of oil resources but have abundant coal reserves, such as the United States and China, *etc.* Coal can be converted into liquid fuels by indirect coal liquefaction (ICL) processes through gasification followed by catalytic conversion of syngas into clean hydrocarbons and oxygenated transportation fuels such as methanol, dimethyl ether, Fischer-Tropsch diesel- or gasoline-like fuels, as extensively

reviewed recently by Larson and Ren [1]. Coal can also be liquefied directly into liquid fuels through direct coal liquefaction (DCL) processes at around 450–500 °C under 15–30 MPa H_2 in a suitable solvent with appropriate catalysts [2-9]. In many processes, the solvent used can facilitate the heat and mass transfer during chemical reactions, and function as a hydrogen donor by shuttling hydrogen from the gas phase to the coal. Catalysts were often used to increase the rates of the desirable reactions such as the cracking, hydrogenation, and oxygen/nitrogen/sulfur removal reactions. Direct coal liquefaction was developed as a commercial process in Germany based on research pioneered by Friedrich Bergius in the 1910s. In addition to the Bergius process (a high-pressure catalytic hydrogenation process), other types of process, represented by the Pott-Bioche solvent dissolving process, were also developed before World War II. Compared to the ICL processes, the DCL processes produce a much larger variety of products (primarily naphtha, a gasoline product) at a higher energy efficiency, although they are disadvantageous with respect to the operating difficulty resulting from the abrasive nature of the coal slurry, the need for expensive hydrogen-donor solvents (such as tetralin), and the difficulties associated with separation of solids from the liquid products. Direct coal liquefaction can be a viable option for the production of synfuels when crude oil prices are above $70–80 per barrel, and it is more attractive in countries like China, which is rich in coal but short of petroleum [2].

Based on the above mentioned two processes, *i.e.*, the Bergius process and the Pott-Bioche solvent dissolving process, a large variety of new DCL processes, such as the SRC-I and SRC-II (Solvent Refined Coal) processes have been developed in many countries, as summarized in Table 1 [3-9].

Table 1. Summary of major DCL processes developed around the world [3-9].

Country	Process	Reactor	Catalyst	Capacity (t/d)	Time
USA	SRC-I	Coal slurry dissolver	—	6	1974
	SRC-II	Coal slurry dissolver	—	50/25	1974-1981
	EDS	Entrained bed	Ni/Mo[c]	250	1979-1983
	H-Coal	Fluidized bed	Co-Mo/Al_2O_3	600	1979-1982
	CTSL	Fluidized bed	Ni/Mo	2	1985-1992
	HTI	Suspended bed	GelCat™	3	1990s
Germany	IGOR	Fixed bed	Red- mud[a], Ni-Mo/Al_2O_3[b]	200	1981-1987
	PYROSOL	Counter-current	—	6	1977-1988
Japan	BCL	Fixed bed[b]	Fe-based[a], Ni-Mo/Al_2O_3[b]	50	1986-1990
	NEDOL	Fluidized bed	Nature pyrite	150	1996-1998
UK	LSE	Stirred tank-type[a], fluidized bed[b]	—	2.5	1983-1995
USSR	CT-5	—	Mo	7	1986-1990
China	Shenhua I	Suspended bed	Fe-based	6	2002-
	Shenhua II	Suspended bed	Fe-based	3,000	2004-

[a] First-stage; [b] Second-stage; [c] Recycled solvent catalytic hydrogenation

The operating parameters and experiment results of four major DCL processes are shown in Table 2 [3-9]. These new DCL processes inherit the advantages of the old processes, but advance the technologies by new catalysts and reactors as well as operating conditions. Nevertheless, due to technical confidentiality, some operating data, especially for small-scale industrial installations are not available from the published literature. As shown in Table 1, China has built a commercial-scale DCL plant (3,000 t/d capacity) in Shenhua (Inner Mongolia, China), and it is the first commercial DCL plant built in the world since World War II [8,10]. The development of the Shenhua DCL process has undergone two stages, from a Bench Scale Unit (BSU) to a pilot-scale Process Development Unit (PDU). A 0.1 t/d BSU facility was built at the end of 2003, and the BSU was tested for approximately 5,000 working hours in total. These experiments validated the feasibility and reliability of the Shenhua DCL process. As a milestone for industrialization of the Shenhua DCL process, the 6 t/d PDU was started-up in Shanghai in September 2004. By the end of 2005, the reliability of the DCL process as well as the equipment was confirmed, and a high conversion rate (90–92%) with hydrogen consumption of 5–7% was achieved. Construction of the demonstration plant (3,000 t/d or about 1 million tons of synfuels per year) started in August 2004 and liquid oils were successfully produced through a trial run in December 2008. This made China the only country in the world to achieve direct coal-to-liquid production at a 1 million-ton-scale. Unfortunately, due to concerns of economics and greenhouse gas emissions the operation of the Shenhua plant was put on hold in June 2009, although it was planned to produce 5 million tons of synfuel per year at a construction cost of $1.46 billion at the plant.

Table 2. The operating parameters and experiment results of some major DCL processes [3-9].

Process	HTI	IGOR	NEDOL	Shenhua
Coal	Shenhua	Xianfeng lignite	Shenhua	Shenhua
Temperature (°C)	440~450	470	465	455
Pressure (MPa)	17	30	18	19
Space velocity (t/m^3/h)	0.24	0.60	0.36	0.70
Conversion (%,daf coal)	93.5	97.5	89.7	91.7
C_4+oils (%, daf coal)	67.2	58.6	52.8	61.4
Residues (%, daf coal)[a]	13.4	11.7	28.1	14.7
Hydrogen consumption (% daf coal)	8.7	11.2	6.1	5.5

[a] Including ash, spent catalyst and un-converted coal

This paper overviews the recent advances in the research on direct coal liquefaction technology with respect to the influencing factors (temperature, solvent, pressure, atmospheres, *etc.*) for DCL reactions, the effects of coal pre-treatments (swelling, thermal treatment, hydrothermal treatment, *etc.*) on DCL, as well as the recent development of multi-staged DCL processes, advanced catalysts and co-liquefaction of coal with biomass.

2. Influencing Factors for DCL

2.1. Temperature

The DCL mechanisms are very complex and not yet known entirely. Generally, the DCL process involves two steps: rupture of the macromolecular structure of coal into radicals fragments at an elevated temperature and stabilization and hydrogenation of those fragments to produce molecules with lower molecular weights [3]. An elevated temperature would crack the coal molecules by thermally rupturing carbon-carbon linkages and enhance the reaction rates. Temperature is thus one of the most important factors that affect free radical formation and the subsequent free radical reactions. These reactions do not normally occur at a low temperature, while at a too high temperature undesirable coking reactions would be dominant. As such, for a specific set of reaction conditions, there exists an optimal temperature. Shui *et al.* [11] established a reaction kinetic model of Shenhua coal liquefaction using a solid acid as catalyst at 375–450 °C. They found that the conversion was increased from 46% at 375 °C to 91% at 450 °C for 1h reaction. However, considerable coke formed at 450 °C. Flatman-Fairs *et al.* [12] demonstrated that an increased liquefaction temperature (from 380 to 400 °C) improved oil yields by enhancing the secondary cleavage reactions, while if the temperature increased to 450 °C, formation of coke by the retrograde reactions was evident. In another study by de Marco Rodriguez *et al.* [13] to liquefy a Spanish sub-bituminous coal in tetralin, the results showed that the formation of free radicals increased greatly as temperature increased, and the optimal temperature for coal liquefaction, in terms of both conversion and quality of the products, was around 425 °C. In a recent study by Cai *et al.* [14], rapid liquefaction of a Chinese lignite coal was performed in waste-tires-derived pyrolysis oil (as a donor solvent) at a temperature ranging from 400 to 800 °C for a residence time from 4.5 to 11.2 s under CH_4 atmosphere without catalyst. The total conversion increased continuously from 4.8% at 400 °C to 25.4% at 750 °C,10 MPa of CH_4 and a residence time of 9.0 s, whereas the conversion and the oil yield decreased as temperature further increased to above 800 °C.

It was shown that the oil yields from a DCL process depended on not only the process temperature, but also the heating rate. For instance, temperature-programmed liquefaction (TPL) appeared to be more effective and superior to rapidly heated liquefaction for low-rank coals [14]. The TPL process consisted of a low-temperature soak at 200 °C for 15 min, and slow heating to the finial temperature at 7 °C/min, followed by a 30 min soak at the final temperature (300~425 °C). By controlling the heating rate, the coals were efficiently liquefied at a controlled rate of pyrolytic cleavage of weak bonds, while minimizing the retrogressive crosslinking of radicals. The coal conversions from the TPL process attained 77–81% at 400 °C, compared with 71–72% in the rapidly heated liquefaction [15]. Similar observations of the beneficial effects of TPL were reported by Huang and Schobert [16], where the low-rank coal conversions in the TPL operations were generally greater than those in the single-stage liquefaction (SSL) and the temperature-staged liquefaction (TSL). For example, in the presence of the ammonium tetrathiomolybdate (ATTM) catalyst and the solvent of Wilsonville middle distillate, the conversions at 400 °C were 84.4, 89.5, and 90.9% for the SSL, TSL, and TPL process, respectively.

2.2. Solvent

In many DCL processes, the role of the solvent is to stabilize the free-radicals by donating hydrogen, promote the cracking of coal macromolecules, and prevent from the condensation and coking of the radicals by diluting the intermediates [15]. Moreover, the solvent used in a DCL process can facilitate the heat and mass transfer for the liquefaction reactions, and function as a hydrogen carrier by shuttling hydrogen from the gas phase to the coal. Coal liquefaction solvents can be classified in four distinct categories based on their effects on coals: specific, non-specific, degrading and reactive solvents. Specific solvents such as pyridine and NMP (*N*-methyl-2-pyrrolidone) can dissolve 20~40% coal at 200 °C. Non-specific solvents such as alcohol, benzene, ether and acetone *etc.* can only dissolve a trace amount of coal at 100 °C. These solvents are electron donors and their dissolution of coal is a physical process as the extraction is normally performed at a low temperature (<200 °C). Chemical extraction processes employing the other two categories of solvents are commonly conducted at higher temperatures. Degrading solvents, such as phenanthridine and anthracene oil *etc.*, can extract coal more than 90% at 400 °C. After extraction, the solvents can be almost totally recovered from the solution. Polymerization of coal fragments may occur in the liquefaction with a degrading solvent, which can be prohibited by supply of high-pressure molecular hydrogen to stabilize the coal fragments facilitated by the solvent's hydrogen transferring and shuttling roles. Reactive solvents are solvents that can react with coal in the liquefaction, such as phenol. DCL solvents may also be classified into donor and non-donor solvents. Typical donor solvents include tetralin, tetrahydrofluoranthene (4HFL), dihydroanthracene (2HAn), *etc.*, and common non-donor solvents are decalin, pyrene (PY), fluoranthene (FL), and anthracene (An), *etc.*

Due to the different properties as discussed above, effects of solvents on DCL are expected to be significant. Mochida and co-workers [17,18] studied the roles of four donor solvents (octahydro-anthracene (8HAn), dodecahydrotriphenylene (12HTp), hexahydroanthracene (6HAn) and 4HFL) in liquefaction of an Australian brown coal under 1.0 MPa N_2 atmosphere. The yields of oil plus asphaltene (O + A) at 450 °C for 5 min and a solvent-to-coal ratio of 1/1 (wt/wt) were 40, 50, 40 and 35 wt% for 4HFL, 8HAn, 12HTp and 6HAn, respectively. It was found that a mixed solvent of 4HFL and 8HAn did not produce any beneficial results. During the process, dehydrogenation of the solvents (e.g., conversion of 4HFL and 8HAn into FL and 4Han/An, respectively) was observed. The effects of non-donor solvents were examined by Sakata *et al.* [19], where pure non-donor solvents such as PY and FL produced a lower oil yield than a donor solvent (4HFL) did. Whereas, a high oil yield was obtained with mixed solvents of 4HFL and PY. Sakata *et al.* [19] believed that a non-donor solvent could swell the coal grains, assist the dispersion of hydrogen donor solvent into coal, and dissolve the coal-derived products to suppress the retrogressive reactions. Hydrogen shutting between the donor and non-donor solvents would also facilitate the hydrogen-transferring process. Such synergistic effects of solvent components in coal liquefaction, achieving a high oil yield at low hydrogen consumption, were also demonstrated by many studies [20-23].

Interestingly, it was found that the use of a non-donor solvent of anthracene or creosote oils in the presence of Mo catalyst precursors led to a higher liquefaction conversion than that of the donor solvent of tetralin [24]. More interestingly, it was demonstrated by many studies [25-27] that water could be an effective co-solvent for coal liquefaction by promoting catalyst dispersion.

2.3. Pressure and Atmosphere

In a DCL process, high pressure is beneficial as it keeps the solvent and products in the liquid phase, prevents coke build-up on the reactor walls and catalyst surface by suppressing the retrogressive reactions, and promotes hydrogenation by maintaining high partial pressure of hydrogen. Nevertheless, economic considerations dictate the use of a lower H_2 pressure in the liquefaction process. With the advances in the DCL technology, particularly in the development of more effective catalysts and solvents, the requirement for high pressure could be relaxed to about 20 MPa [3-9]. It was even demonstrated that when a suitable solvent with an enough high boiling point was used, coal could be liquefied under atmospheric pressure [6], although most of the products were heavy fractions and the oil yield was only about 10%. In the presence of a good donor solvent, coal liquefaction could proceed under relatively lower pressure, although coal conversions could be improved appreciably by increasing the operating pressure. When liquefaction reached a certain degree of extent, however, further increasing the pressure had little effect on the oil yields [17]. Similarly, it was found that the liquefaction yields were almost unchanged as the pressure increased from 14.7 to 18.6 MPa [28]. In a study by Cai *et al.* [14], the total conversions were found to only slightly increase from 25.4% to 26.1% as the process pressure was increased from 10 to 15 MPa.

Although it was found that when using a good donor solvent in coal liquefaction, a high conversion could be obtained under N_2 atmosphere [17], most DCL processes operated under a high-pressure hydrogen atmosphere. Assisted by the hydrogen shuttling effects of the liquefaction solvents, the gaseous phase hydrogen can be transferred into coal. The hydrogen as a capping agent can stabilize the radicals/fragments to form liquid products and suppress the coke formation reactions in the process. It was estimated that roughly 30% of the production cost for a DCL process is associated with hydrogen generation [29]. Molecular hydrogen itself is a poor capping agent because of the stability of the H-H bond, but the H_2 molecules can be dissociated into reactive atomic hydrogen under high severity conditions and in the presence of an appropriate catalyst. There is considerable interest in liquefaction of coals using an alternative gas source, such as CO, CO-H_2 mixtures, CO-H_2O, H_2-H_2O, syngas-H_2O, N_2 and CH_4, *etc.* It was noted that low-rank coals can be converted to useful products at a high yield by reaction with CO-H_2 in the presence of alkaline catalysts [30]. Recently aqueous systems appear to attract increasing attention, although the use of H_2O in a DCL process has shown controversial effects. The negative effects of water addition in a liquefaction process is in agreement with the common perception that water is detrimental to catalytic hydro-processing by decreasing the activity of some catalysts and promoting CO_2 formation. In contrast, water as a DCL solvent exhibited some positive effects [31-33] particularly in CO atmosphere. Shui *et al.* [31] observed that with water as a solvent, the liquefaction conversion and (oil + gas) yields in CO atmosphere were higher than those in H_2 or N_2 atmosphere, although the yields were still lower than those in the system of tetralin-H_2. Watanabe *et al.* [32,33] reported that in the liquefaction with the catalyst of ($Fe(CO)_5$ + S), a high coal conversion could be obtained in CO-H_2O systems at a rather lower temperature of 375 °C. It might be ascribed to the formation of hydrogen *in situ* by the gas-water shift reaction, where *in situ* hydrogen was more reactive for coal liquefaction than the pressurized hydrogen [30,32,33]. Hulston *et al.* [34] found that when water was used as a solvent, the maximum conversion was observed at a water/coal ratio of 2.5:1 (wt/wt) and a CO/H_2 ratio of 1:2 (vol./vol.).

Rapid liquefaction of a lignite coal under methane atmosphere was also studied in a tubular reactor at a temperature ranging from 400 to 800 °C for a residence time ranging from 4.5 to 11.2 s and 10–15 MPa without catalyst [14]. The results indicated that there were synergistic effects between coal and methane at temperatures higher than 600 °C, the oil yields reached a maximum of 22 wt% (daf) at 750 °C in the rapid liquefaction for 9.0 s. The effectiveness of CH_4 in coal liquefaction was improved further by co-presence of hydrogen according to the study by Yang *et al.* [35], where the coal conversion attained as high as 51.5% in a gas mixture of CH_4-H_2, compared with only 27% under CH_4 atmosphere alone. As discussed before, a sulfided metallic catalyst and a hydrogen donor solvent are two essentials for a DCL process, while the presence of H_2S in the gas phase could promote the hydrogen exchange and the donor ability of some solvents [36].

3. Effects of Coal Pretreatment on DCL

3.1. Swelling Treatment

As discussed in the previous section on the effects of solvent, some mixed solvents exhibited excellent performance in the DCL, achieving a high oil yield at a low hydrogen-consumption. For example, the mixture of a non-donor solvent and a donor solvent showed synergistic effects on DCL, producing higher oil yields than any of its component solvent [19-23]. It was believed that the non-donor solvent could swell the coal grains, assist the dispersion of hydrogen donor solvent into coal, and dissolve the coal-derived products to suppress retrogressive reactions [19].

Solvent swelling of a coal could selectively disrupt some hydrogen bonds and increase the mobility of small molecules associated with the macromolecular network of the coal. This process could facilitate self-donation of the coal-bound hydrogen, thus suppressing the initial retrogressive reactions and enhancing the coal reactivity. By swelling pretreatment, coal molecules can be dissociated, rearranged and re-associated in lower free energy conformations, or probably in a different molecular structure. The swelling solvents may break weaker bonds, create macro-pores or enhance the coal porosity, and hence facilitate the dispersion of the catalyst onto the coal structure, and more importantly assist the dispersion of the hydrogen donor solvent into the coal [37-39]. The yields of liquefaction products were strongly dependent on the type of swelling solvent used. A recent study [40] demonstrated effectiveness of a new swelling-liquefaction combined technology (SLCT), where the coal was pre-swollen in tetralin or *N*-methyl-2-pyrrolidinine (NMP) for 4 h at a temperature from room temperature up to 160 °C before being heated to 400 °C for 30 min for liquefaction. The pre-swelling treatment with NMP did not yield any positive effects on coal conversion and oil yields, but the pre-swelling treatment with tetralin did improve the coal liquefaction significantly. Liquefaction of the 120 °C/tetralin pre-swollen Shenhua coal produced 67.6% of conversion and 26.8% of (oil + gas) yield, compared with 55.5% and 20.8%, respectively, from the liquefaction of the raw coal. Swelling contact time was found to have a marked effect upon the coal conversion, but the effect was strongly dependent on the type of swelling solvent too [41]. With V1074 as the liquefaction solvent and THF and isopropanol as swelling solvents, the coal conversion increased with increasing the swelling treatment time up to 12 h, whereas when 1-methylnaphthalene (1-MN) was the reaction solvent, the coal conversion decreased with increasing swelling time [41], wherein V1074 was a coal-derived solvent, supplied by Amoco Oil Company, having a nominal boiling range of 343–482 °C and

elemental compositions of 87.2% C, 9.7% H, 0.5% N, 2.5% O, and 0.04% S. In addition, the effects of swelling pretreatment were dependent on the type of coals in liquefaction [42]. According to the work of Artok *et al.* [42], the effects of pre-swelling treatment on different coals were distinct. Pyridine pretreatment of Blind Canyon coal greatly enhanced the oil yield from the catalytic temperature-staged liquefaction of the coal, while the pretreatment of Big Brown coal led to little or no improvement in oil yields.

Although it is commonly believed that the swelling solvents can enhance the coal porosity, and improve the dispersion of the catalyst onto the coal structure as discussed above [37-39], negative impacts of the swelling solvents were also observed [41,43,44]. Shui *et al.* [44] demonstrated that the presence of swelling solvents in the swollen coal was detrimental for the subsequent liquefaction of the swollen coal. It was observed that removing the swelling solvents led to an increased liquefaction conversion and oil yields for the swollen coals. For example, the removal of the swelling solvent of NMP increased the conversion and (oil + gas) yield from 61% and 4.1% to 65% and 20.8%, respectively.

3.2. Thermal and hydro-Thermal Treatment

Preheating treatment might be the simplest and most practical measure to improve DCL conversion and yields. Coal can be preheated in a swelling solvent, steam or water. Direct preheating treatment, *i.e.*, drying a coal, was found to be detrimental for DCL. Miknis *et al.* [39] demonstrated that liquefaction of thermally dried coals led to a decrease in the amount of liquid products. For most coals tested, there is a general trend of decreased liquefaction conversion with increasing the percentage of water removed. Moreover, retrogressive reactions responsible for coke formation would be favored when a coal is oxidized during drying in air, so it is desirable to dry the coal in vacuum or under an inert atmosphere and a lower temperature. In contrast to the drying in air, preheating treatment in steam was found to be beneficial for the DCL of coals [45]. Preheating treatment of coal in sub-critical steam at 385 °C (by rapid heating) for 15 min increased the oil yield in the subsequent liquefaction of the coal from 12.5% for the raw coal to 29% for the steam-treated coal [45]. Again, the stream pretreated coal must be prevented from exposure to air, as the exposure would decrease the oil yield and the liquefaction conversion to almost the same levels as those of the un-treated coal.

Hydrothermal treatment (namely the treatment in hot-compressed water) at a relatively low temperature proved to be an effective measure for direct coal liquefaction. Shui *et al.* [46] observed that the extraction yields using CS_2/*N*-methyl-2-pyrrolidinine (NMP) increased significantly by hydro-thermal treatment of low rank coals at 150–240 °C. It was found that during the hydrothermal treatment, the oxygen functional groups such hydroxyl group were removed and the hydrogen bonds in macromolecular network of coal could be ruptured. Hydrothermal treatment of coal not only increased its solubility in the mixed solvent, but dissociated the heavier constituents of the extract [47]. It was observed that as the hydrothermal treatment temperature increased, the amount of all carbon-oxygen forms of structure in the lignites decreased, and the relative amount of quaternary-*N* decreased accompanied by an increase in the amount of pyridinic-*N* [48]. Wang *et al.* [49] studied the effects of hydrothermal treatment at 150–350 °C on DCL of Shenhua coal in the solvent of tetralin catalyzed by FeS. The results showed that the hydrothermal treatment at 250–300 °C improved the liquefaction

conversion and the yields of asphaltene (AS) and pre-asphaltene (PS), while it slightly reduced the (oil + gas) yields. It was shown that 300 °C appeared to be the optimal hydrothermal treatment temperature, as negative effects on the coal conversion were observed at a temperature above 300 °C. For instance, the hydrothermal treatment of Shenhua coal at 350 °C decreased the total conversion drastically from 60.5% for the raw coal to 39.8% for the treated coal.

4. Multi-stage DCL Processes

The major DCL processes as shown in Table 1 may be classified into single-stage processes including the SRC, EDS, H-Coal, Pryosal and LSE, and multi-stage (mostly two-stage) processes. Multi-stage processes were believed to be advantageous as they could obtain higher conversions and oil yields than the single-stage processes [18,31,50-53]. Mechanically, the advantages of multi-stage processes over single-stage processes are accountable by the effects of *in situ* thermal/hydrothermal pre-treatment and the improved hydrogen transfer [52,54,55], as discussed before. Priyanto *et al*. [50] reported a two-stage liquefaction process with Tanito Harum coal (Indonesian sub-bituminous coal) under the hydrogen pressure of 15 MPa using 10 wt% Fe-10 wt% Ni catalyst supported on carbon nanoparticles. Under the optimal conditions of the two stage liquefaction: 380 °C for 15 min in the first stage and 450 °C for 105 min in the second stage, the maximum oil yield was obtained at 80 and 66 wt % (daf coal base) with or without H-donor solvent, respectively. The conversion of H-donor solvent (tetralin) after the liquefaction was much lower (13%) than that of the single-stage liquefaction (21%). In addition, the residue yield was much lower (9 wt%) than that of the single-stage (15 wt%) in the solvent-free liquefaction. The two-stage liquefaction also produced an oil yield 10 wt% higher than that of the single-stage liquefaction with a reduced hydrogen-consumption under the optimal conditions in the solvent-free liquefaction. Normally, combination of a lower temperature stage (<400 °C) with a higher temperature stage (around 450 °C) was effective for improving the oil yields and suppressing the yields of gas and heavy products [51,52]. Mochida *et al.* [53] reported an interesting multi-stage liquefaction process consisting of coal de-ashing pre-treatment, solvent-mediated hydrogen-transfer dissolution, and catalytic hydro-cracking steps. The process could achieve a higher oil yield and enable recovery and reuse of the catalysts without severe deactivation.

5. DCL Catalysts

Development of high performance catalysts is the key to the development of almost all DCL processes, and not surprisingly, almost all of the metallic elements in the periodic table have been tested for DCL [3]. Catalysts were employed in almost all of the DCL processes developed. Although some processes claimed running without catalyst, most coals themselves contain a significant amount of minerals such as pyrite and iron oxides that could play a role in the DCL process as a catalyst. Iron-based catalysts, such as pyrite (FeS_2), troilite (FeS), pyrrhotite ($Fe_{1-x}S$), iron oxide, iron sulfate, iron hydroxide and other iron resources, have been studied extensively due to their low costs and environmental tolerance. It is widely accepted that pyrrhotite is the most active form for iron sulfide catalysts. The iron-based catalysts could promote coal pyrolysis by markedly reducing the pyrolysis activation energy [56]. The major role of an iron-based catalyst in DCL is to promote the formation of activated hydrogen atoms and accelerate the secondary distribution of hydrogen atoms in the whole

reaction system [60]. The activity of an Fe-based catalyst was influenced by the loading amount, the preparation methods, the dispersion states, the solvents, and the coal-containing minerals, *etc.* It was widely recognized that a highly dispersed catalyst can be superior to a supported catalyst, because the dispersed catalyst has an intimate contact with the surface of coal particles, which facilitates the activation and transfer of hydrogen to the coal-derived fragments and reactive sites. Accordingly, finer particles and a higher dispersion of the catalyst species would lead to a higher catalytic activity [57-60]. Liu *et al.* [58] tested DCL with an *in situ* impregnated iron-sulfide catalyst, where the coal was mixed with Na_2S solution, followed by the addition of $FeCl_3$ solution, washing, filtration and drying. This highly dispersed catalyst even of a low loadings (<0.5 wt%) resulted in a high level of coal conversion. Hirano *et al.* [60] found that pulverized pyrite and α-FeOOH both produced a higher conversion, an increased oil yield and a larger hydrogen-consumption than the raw pyrite did. Kaneko *et al.* [61] reported that sulfided limonite and α- or γ-FeOOH were active catalysts for coal liquefaction, and γ-FeOOH exhibited the best catalytic activity due to the transformation into pyrrhotite with smaller crystallite size under the liquefaction conditions. The liquefaction of Yallourn coal under 7.5 MPa of initial hydrogen at 450 °C for 1 h with γ-FeOOH produced an oil yield of approximately 50 wt%.

In addition to the Fe-based catalysts discussed above, Mo, Co and Ru were also tested as the catalysts for DCL. Ikenaga *et al.* [57] reported that highly dispersed catalysts such as $Mo(CO)_6$-S and $Ru_3(CO)_{12}$ remarkably increased the oil yields. Song *et al.* [62] found that a bimetallic catalyst generated from $Mo_2Co_2S_4(Cp)_2(CO)_2$ [Cp = cyclopentadiene] was substantially more active than the physical mixture of the two metal carbonyls, $Mo(CO)_6$ + $Co_2(CO)_8$, or the mixture plus sulfur. Hulston *et al.* [63] reported that aqueous solutions of nickel acetate and ammonium heptamolybdate pre-impregnated on brown coals were very active for DCL, leading to a very high conversion (92%) at 400 °C even in the absence of solvent. Their results also implied that there were synergistic effects between the Ni and Mo catalysts. Another type of novel catalysts for DCL is SO_4^{2-}/M_xO_y solid acid, such as SO_4^{2-}/Fe_2O_3 and SO_4^{2-}/ZrO_2 [11,64,65]. The solid acid could be a bi-functional catalyst for pyrolysis and hydrogenation. The use of SO_4^{2-}/ZrO_2 catalyst in the DCL of Shenhua coal at 400 °C and 4.0 MPa H_2 resulted in a coal conversion and (gas + oil) yield, up to 76.3% and 62.5%, respectively, much higher than those obtained with FeS or (FeS + S) catalyst under the same conditions.

6. Co-liquefaction of Coal with Biomass

Co-liquefaction of coal with biomass (agricultural/forestry residues and cellulosic waste materials) has gained increasing research interest due to the growing concerns over greenhouse gas emissions and environmental issues related to fossil fuels. Another motivation of the research on co-liquefaction of coal with biomass may be the potential synergistic effects between biomass and coal during liquefaction [66-68]. These studies demonstrated that co-liquefaction of coal with biomass-type wastes has a positive and synergetic effect, improving the yields and quality (e.g., H/C ratio) of the liquid products produced from coal under milder conditions of temperature and pressure.

Co-liquefaction of biomass and coal in supercritical water was tested at 673 K and 25 MPa by Matsumura *et al.* [66]. It was found that co-liquefaction of low-rank coals and cellulose in the supercritical water medium was beneficial owing to the *in situ* generated hydrogen by supercritical water gasification

of biomass, resulting in enhanced coal conversion and increased yields/quality of the liquefaction products. Altieri *et al.* [67] studied co-liquefaction of a bituminous coal (Illinois #6) and lignin at 400 °C in tetralin. The co-liquefaction produced 30% yield of benzene soluble, compared with only 10% for the liquefaction of the coal alone. Lignin and coal in co-liquefaction were found to be synergistic too in another research by Lalvani *et al.* [68]. Karaca *et al.* [69-71] investigated co-liquefaction of a Turkish lignite with a cellulosic waste material in tetralin at different conditions. The highest increase in total conversion was obtained by co-processing the lignite with sawdust at 325 °C. Rafiqul *et al.* [72] examined hydro-liquefaction of a Chinese bituminous coal and bagasse at temperatures of 350–450 °C for 15–45 min under hydrogen of a cold pressure of 300–700 psig. The addition of bagasse to the coal liquefaction was found to be beneficial. The oil yield reached 48% at the optimum conditions (420 °C, 500 psig of cold hydrogen pressure and 40 min of reaction time). Co-liquefaction of micro algae with coal was studied under H_2 at 5 MPa (cold pressure) in 1-methyl-naphthalene at 350–400 °C for 60 min with various catalysts [73]. Co-liquefaction of *Chorella* algae and Yallourn coal (1:1 wt/wt) produced 99.8% of the conversion and 65.5% of hexane-soluble oil fraction at 400 °C with $Fe(CO)_5$ catalyst at S/Fe = 4. It was shown that sulfided $Ru_3(CO)_{12}$ was also effective for the co-liquefaction of micro algae with coal. Stiller *et al.* [74] researched the liquefaction of Blind Canyon seam coal in the presence of biomass as the co-liquefaction agent (sawdust, horse manure, cow manure or commercial Super Manure) at 350 °C under 1,000 psig hydrogen (cold pressure) in tetralin. The overall conversion and liquid yields were both higher in the co-liquefaction than those in the liquefaction of coal or the individual biomass material.

In summary, co-liquefaction of coal with biomass could moderate the reaction conditions of coal liquefaction due to the synergistic effects between coal and biomass, and improve the quality and yields of liquid products. However, so far the mechanism behind the synergistic effects of co-liquefaction is yet to be clarified, so more research shall be conducted.

7. Conclusions

In this article, some recent advances in the DCL technology were overviewed from various perspectives, including the influencing factors for the DCL reactions (temperature, solvent, pressure, atmospheres, *etc.*), the effects of coal pre-treatments for DCL (swelling, thermal treatment, hydrothermal treatment, *etc.*), as well as some recent development in multi-stage DCL processes, DCL catalysts and co-liquefaction of coal with biomass. Overall, although many commercialized processes have been developed in the US, Europe, Japan and China, the optimization of the operating conditions for these DCL processes is still the focus of many studies.

Coal pre-treatment such as swelling, and thermal/hydrothermal pre-treatment proved to be an effective measure for DCL. Multi-stage processes were believed to be advantageous as they could obtain higher conversions and oil yields than the single-stage processes did. High performance catalysts remain the key to the efficiencies of almost all DCL processes. In addition to the common Fe-based catalysts, Mo, Co and Ru as well as SO_4^{2-}/M_xO_y solid acids were also demonstrated effective for DCL.

Co-liquefaction of coal with biomass-type wastes has positive and synergetic effects on the liquefaction of coal. It can improve the yields and quality (e.g., H/C ratio) of the liquid products from coal under milder conditions of temperature and pressure.

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