8 Summary

In this thesis, a novel oxidative approach for the conversion of coal, particularly lignite, with activated hydrogen peroxide as oxidative species under mild conditions was explored.

At the beginning, the optimum reaction temperature for the liquefaction of lignite mediated by the \([\text{Al(H}_2\text{O)}_6]^{3+}/\text{H}_2\text{O}_2\) system was explored. It was discovered that the conversion of coal depends strongly on the reaction temperature. The optimum temperature for this methodology is about 65-70 °C where mostly the mineral matter and low amounts of insoluble acidic compounds are remaining. Surprisingly, the obtained product oil samples consist of mostly saturated compounds, comprising not only fragments from coal but also about 35 % products from 2-Me-THF degradation which seems to dissolve the coal fragments.

The next chapter discussed the optimum process duration for the conversion of lignite mediated by the \([\text{Al(H}_2\text{O)}_6]^{3+}/\text{H}_2\text{O}_2\) system at 65 °C. Herein, it was shown that the main conversion of lignite takes place within the first 30 min of process duration. Furthermore, the calculation of comprising 2-Me-THF/coal/OH groups within the new formed product oil samples revealed that the conversion of coal is completed after 120 – 150 min process duration and the ratios of the participating compounds within the product oil do not change afterwards.

More interesting results were obtained from studying the effect of solvent for this reaction system. Pretests showed that no product oil samples were obtained from reactions in
methanol, ethanol and water. Furthermore, the soluble products comprised high amounts of remaining catalysts. Therefore, the effect of the solvent was studied for coal benefication processes. Herein, the reaction conditions remained, only the process duration was changed to 5, 10 and 30 minutes. The results showed that processing lignite in methanol and water leaves most of the aromatic structure intact, whereas reaction in 2-Me-THF and ethanol revealed a dramatic loss of aromatic compounds. All obtained lignite residue samples showed improved thermal degradation behavior.

Since the structure of lignite residue samples obtained from process in methanol were mostly untouched, hydrodeoxygenation experiments were performed to investigate whether further upgrading of the lignite samples is possible. The HDO experiments in presence of Ni₅P/SiO₂ catalysts presented promising first results. The complex coal structure could be further cleft into smaller fragments, such as phenols, benzenes, naphthenes, hydrocarbons.

In addition, the capability of the [Al(H₂O)₆]³⁺/H₂O₂ system on higher coal ranks was explored. The experiments showed that only high volatile bituminous coal (here: “Gasflammmkohle”) was converted in low amounts. Coals of higher maturity were mostly unaffected and the very low yields of derived product oil samples consist of 2-Me-THF degradation products. Only “Gasflammmkohle” showed improved properties regarding thermal degradation.

The last chapters of this thesis are dedicated to the mechanistic investigation into the reaction system. Herein, the formed radical species were determined by EPR spectroscopy and variable temperature dynamic NMR studies were performed as well to investigate the proton exchange between activated hydrogen peroxide and water within the [Al(H₂O)₆]³⁺/H₂O₂ system.
By means of EPR spectroscopy, it was shown that aluminum, gallium and indium nitrate activate hydrogen peroxide and generate hydroxyl and perhydroxyl radicals, with gallium being less effective than aluminum and indium. Surprisingly, only hydroxyl radical species were detected for the reaction systems using aluminum, gallium and indium perchlorate as activator. Moreover, it was confirmed that 2-Me-THF and methanol act as a radical scavengers, whereas the fast formation of the hydroxymethyl radical results in its majority of all radical species found, which explains the milder oxidation of coal in methanol as solvent.

Additional D-NMR studies support the obtained data from EPR spectroscopy by showing great differences for the proton exchange between hydrogen and water for the perchlorate, nitrate and chloride anion. Herein, the perchlorate anion shows great potential for activating proton exchange whereas nitrate and chloride anion are much less effective. Minor difference between the various cations (Al\(^{3+}\), Ga\(^{3+}\), In\(^{3+}\)) have been also detected. The fastest exchange was observed for the Ga\(^{3+}\) system, followed by indium and aluminum. The size of the cations and their differences in the 1\(^{st}\) and/or 2\(^{nd}\) coordination sphere only slightly affects the proton exchange whereas the anions reveal a greater influence due to their different abilities in stabilizing or weakening the hydrogen bonds in H\(_2\)O-H\(_2\)O molecules.

Overall, the conversion of coal under low-severity conditions mediated by the [Al(H\(_2\)O)\(_6\)]\(^{3+}\)/H\(_2\)O\(_2\) system was explored within this thesis. It was shown that lignite can be effectively converted, either into an oil or soluble product, dependent on the choice of solvent. However, this thesis suggests that the conversion of coal mediated by the [Al(H\(_2\)O)\(_6\)]\(^{3+}\)/H\(_2\)O\(_2\) system seems to be more suitable for coal beneficication processes, either to improve chemical and physical properties, or combined with an additional further upgrading, such as HDO process for the production of fine chemicals.