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主　論　文　の　要　旨

論文題目　Development of carbon capture process using a flexible metal–organic framework and critical path method considering stochastic durations
(柔軟な金属有機構造体を用いた二酸化炭素回収プロセスおよび処理時間の不確実性を考慮したクリティカルパス法の開発)

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論　文　内　容　の　要　旨

Intergovernmental Panel on Climate Change (IPCC) indicates that global warming caused by the anthropogenic carbon dioxide (CO_2) is a growing concern, and that unless CO_2 emissions are reduced to net zero by the 2050s, severe impacts of climate change on humankind will be inevitable. Carbon capture utilization and storage (CCUS), which captures CO_2 from exhaust gases and the atmosphere, sequestrates it by storage, and converts it to valuable resources for reuse, is one of the approaches to contribute to the CO_2 reduction. However, cost must be reduced to realize economically feasible CCUS systems.

Since thermal power plants generate about 30% of anthropogenic CO_2 emissions, a cost-efficient post-combustion CO_2 capture process is essential for the CCUS systems. Post-combustion CO_2 capture processes include absorption, adsorption, and membrane separation. Currently, absorption processes are the most established, but they require a large amount of energy to regenerate the absorbent materials. For this reason, adsorption processes are promising because they require less energy to for regeneration than absorptive processes due to their lower CO_2 affinity. While various CO_2 adsorbents have been developed, metal–organic frameworks (MOFs) are new adsorbents that show desirable properties by selecting combinations of organic ligands and metal ions that consist the MOF crystals. Among many MOFs, flexible MOFs have attracted attention because of their unique property of changing structure before and after adsorption. Due to this property, flexible MOFs show remarkable performance for CO_2 separation — high working capacity and selectivity, step-type adsorption isotherm, and low heat of adsorption. However, they have not yet been analyzed using a process simulation, and the performance of the CO_2 capture process using the flexible MOFs is unknown.

In this thesis, adsorption isotherms were modeled for the CO_2 capture process using a flexible MOF. Adsorption isotherms data using elastic layer-structured metal–organic framework-11 (ELM-11), one of the typical flexible MOFs, were measured by my collaborator, Nippon Steel Corporation. I modeled the stepwise and hysteresis adsorption isotherms which were confirmed to fit well to the data.

The process simulation using ELM-11 was performed using a rigorous model with partial differential-algebraic equations (PDAEs). Since PDAEs may not converge with rapid change in derivatives in a short time, the process simulation with ELM-11 is computationally challenging because the stepwise adsorption isotherms can cause rapid changes in CO_2 partial pressure, and the isotherms hysteresis can cause discrete changes in adsorption amount of CO_2. In this thesis, these problems were solved by applying several numerical techniques. My study is the first to simulate the process with stepwise and hysteresis adsorption isotherms. Note that the operating conditions, such as adsorption time, desorption time, and desorption pressure, were systematically determined for a fair evaluation.

The results of the process simulation revealed the following. First, the CO_2 recovery rate highly depends on feed pressure and temperature. By analyzing the mechanism how the recovery rate is determined, I proposed a simple and useful equation to estimate the recovery rate from feed pressure and temperature without running the simulation. Second, due to the high CO_2 selectivity of ELM-11, the purity of recovered CO_2 is very high (>99%). Third, ELM-11 shows superior CO_2 recovery, productivity, and power consumption compared to zeolite 13X, a conventional adsorbent. In particular, the stepwise desorption isotherm shortens the desorption time, and productivity is about 4.5 times higher than zeolite 13X. The above results demonstrate that the CO_2 separation process using ELM-11 is promising.

On the other hand, various studies have applied mathematical programming to optimize the economics of CCUS systems. One of such approaches is a resource-constrained project scheduling (RCPS) method, which optimizes system schedules under resource constraints, such as workforces and funds. As far as I know, this method has not yet been applied to CCUS systems. Among the RCPS methods, Critical Path Method (CPM) is a popular method and has been used for various systems scheduling, such as building construction projects, factory management, etc. CPM assumes that each task in the system has a given duration of processing time, which can be reduced by allocating the cost. In the system, the optimum cost allocation is obtained by solving an optimization problem in which the decision variable is cost and the objective function is the minimization of the project completion time. Since the classical CPM assumes that the task durations are fixed values, it cannot account for uncertainties in task durations. This can be a bottleneck for applications in CCUS, which are expected to include duration uncertainties in tasks such as generating electricity from natural energy, transporting synthesized fuel from the recovered CO_2, running CO_2 adsorption processes, etc. Therefore, the optimization results can be unreliable if the conventional CPM is applied without resolving this critical problem.

I proposed an advanced CPM, which can account for the uncertainty in task durations by expressing them using histograms obtained from historical operation data. I proposed three formulations, all of which have their advantages. The first, Task-Oriented Formulation, has two different ways to improve the task durations by allocating costs and can find more flexible ways of allocating costs than the conventional CPM, which has only one way to improve the durations. However, this method requires many decision variables and takes a long time to solve the optimization problem. The second, Path-oriented Formulation, significantly decreases the number of decision variables compared to Task-Oriented Formulation, instead of limiting the improving ways of task durations to one. The third, Path-oriented Formulation with local search, further reduces the number of decision variables by applying the local search method to Path-Oriented Formulation. This method does not guarantee an optimal solution depending on a range of local searches. The three methods above involve trade-offs between computation time, flexibility in cost allocation methods, and solution accuracy. They should be chosen according to the size of the target system.

Note that my formulation of the optimization problem is mixed-integer linear programming (MILP), which can be solved by an algorithm that guarantees a solution, such as the branch and bound method.

In conclusion, this thesis provides important insights into the realization of CCUS systems to improving the economics. The CO_2 separation process with the flexible MOF allows high productivity, high product purity, and low power consumption. Furthermore, the proposed RCPS methods for designing and operating CCUS systems, which takes into account the uncertainty in task durations, maximizes the productivity of the systems under the cost constraints.