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Making processes work

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ABSTRACT

Chemical processes and their flow-sheets are systems and as with all systems one cannot optimise each part alone and expect to get an optimal process. One also has to take into account the connections and interactions between the parts of the systems in order to achieve the global optimum. In this paper fundamental thermodynamics will be used to show how to achieve an optimal solution. A coal-to-liquids (CTL) process will be used to illustrate the method.

The overall material balance for a process will be looked at first. This material balance must include the constraints such as the energy (heat and work) balance and thus must include the feed streams that supply utilities, such as heat and electricity to the process. The best material balance ensures that as much of the feed material ends up in the product. In the examples discussed, focus will be on ensuring that as much of the carbon in the feed as possible ends up in the hydrocarbon product; the carbon from the feed that does not report to the product is emitted from the process as CO_2 which is undesirable for a number of reasons.

The resulting overall material balance is then regarded as the process target, since it is the "best" material balance. Furthermore, the manner in which energy (heat and work) is added or removed from a process, affects the material balance by introducing irreversibilities. The greater these irreversibilities are, the further the process operates from the process target, implying that the process produces more CO_2 per mole of product produced.

Many processes, such as CTL, require substantial quantities of work to be added. It is shown that this may be done by designing the overall process such that the process itself is effectively a heat engine. Thus heat at high temperature is added in an endothermic, high temperature sub-process (e.g. gasification) and (less) heat is rejected at a lower temperature from an exothermic, low temperature sub-process (e.g. Fischer–Tropsch synthesis). Just as in a heat engine, there is a relationship between the values of the high and low temperatures, the quantities of heat flowing in and out of the sub processes and the amount of work added to the overall process. One can note that any stream has an enthalpy and a temperature and these two together can be used to describe the work content of this stream.

The Carnot temperature for each sub-process is defined as the temperature at which the heat added to the sub-process takes with it the work content required by the sub-process. The bigger the difference between the actual operating temperature and the Carnot temperature, the more irreversible the process is and the further away the process operates from the process target.

A CTL process has been chosen to apply the methods in order to obtain the process target and the overall material balances for different options. It is shown that there are different ways of arranging the heat engine for CTL, for example indirect or direct liquefaction, and that the direct route has higher carbon efficiency than the indirect route. However it is shown that one can use the ideas in the paper to synthesise a new route for CTL where rather than gasifying to syngas, one gasifies to hydrogen and carbon dioxide followed by the FT synthesis reaction. In this way one can show that this indirect CTL route is nearly as efficient as the direct route.

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1. Introduction

Historically, chemical process flow-sheets have been chosen based on the experience of the design engineers. Subsequent to this much effort has gone into the design and optimisation of the individual units that make up the chosen flow-sheet. While this addresses the optimal design and operation of the individual units, it does not take account of the interaction between the units. An assemblage of optimal units does not ensure that an optimal flow-sheet and hence an optimal process, has been achieved. This paper is focused towards looking at the interaction between the units, namely the system.

This focus on the units is probably a result of the history of chemical engineering, which grew out of what was called unit operations (Perkins, 2003). This arose during the industrial revolution where it was realised that different processes had many steps in common, e.g. reaction, separation and mixing, and these were referred to as unit operations and chemical engineering grew out of these areas and individuals became experts in each of these areas separately. No-one however seemed to have become an expert in putting these areas together, that is, in the system as a whole and the interactions between the units. Thus most chemical engineers still specialise in individual unit operations such as reactor engineering, distillation and mixing.

With the advent of the Second World War suddenly new unit operations needed to be rapidly designed without much prior knowledge. To do this, teams of physicists, chemists and chemical engineers worked together using all the scientific knowledge at their disposal. An example of this was the need for large quantities of polythene as insulators for radar equipment. To do this with the technology of the time, reactors up to 1000 bar, an extremely high pressure for the time, had to be designed. The need for enriched uranium for the atomic bomb was another such project. Out of all of this grew what was called chemical engineering science in which the units could be designed using sophisticated science (Perkins, 2003). Less emphasis has been put into the flow-sheet design. As processes became ever more complicated the flow-sheet typically grew generically rather than based on any scientific basis.

This neglect of the flow-sheet was probably due to the fact that energy was cheap and there was no real incentive to look at the process as a whole. The situation has now changed significantly because of the high cost of energy, the limit on the long term availability of fossil fuels and the effect of carbon dioxide emissions on climate change. Suddenly one needs to look at all possible ways of improving the efficiency of the plant and certainly improving the flow-sheet could be an important aspect of this. What will be done in this paper could have been done a hundred years ago but probably for the reasons mentioned above has not been done.

With the advent of the digital computer many of the more complex situations can and have been modelled leading to better and more accurate design methods (Dowling and Biegler, 2015; Farkas et al., 2005; Rodrigues and Minceva, 2005; Westerberg, 2004). Most of these are however based on simulations rather than synthesis. Thus there are very complex design packages such as Aspen Plus that are based on the simulation of individual units and doing material and energy balances on the chosen flow-sheet. One is then able to do some optimisation by doing a series of simulations and finding the best. The question then remains how good was the chosen flow-sheet?

Other researchers have been looking at flow-sheet development and improvement using computer programmes. What is generally done is to set up a complicated superstructure of individual units trying to encompass all the possibilities that the designer thinks might be important. Then computer optimisation methods such as Mixed Integer Non-Linear Programming (MINLP) are used to find the best solution (Achenie and Biegler, 1990; Farkas et al., 2005; Grossmann, 1985; Lu and Motard, 1985; Yeomans and Grossmann, 1999). This is actually a sophisticated computer method based on repeated simulations and depends on how good the original chosen superstructure was (the answers achieved can only be as good as the superstructure chosen) and also quite importantly did the computer programme converge and if so was it on the best solution?

Another factor that has led to inefficiencies in chemical processes is the sequential management processes which sometimes use stage gates and which are based on the assumption of a fairly linear progression of detail in the development of a process or flow-sheet (Biegler et al., 1997; Westerberg, 2004). Hence often the chemistry is developed in the laboratory. Very important decisions are made regarding the chemical routes to use and factors such as the operating temperatures and pressure of the laboratory reactor and thus often, by implication, the process operating conditions. There is often no or very little interaction between the design or process engineers and the people in the laboratory that allows one to evaluate the implications of the decisions made in the laboratory on the performance or efficiency the final plant. As will be shown via the examples in this paper, these decisions are critical and can set the limits of performance for the process.

In this paper the problem is approached quite differently, not just based on simulation but rather on analysis and synthesis. What is addressed is what the best possible performance of a plant is? For instance what is its highest possible efficiency? This is called a *target* and one can look at different options and how they affect the target. In this paper coal-to-liquids (CTL) plants will be looked at as an example and it will be seen how the synthesis techniques can be used to examine different options and find targets for them. At this stage discussion of how to then synthesise plants that can approximate these targets will not be undertaken but techniques to do this have been developed (Fox et al., 2013, 2014).

2. The tools

There are three fundamental tools that can be used to synthesise and analyse processes (Patel et al., 2007):

- Material balance
- Energy balance
- Entropy/work balance

Historically these tools have not been used for synthesis, but rather mainly for analysis after the process flow-sheet has been virtually completed in order to check that everything has been accounted for. Yet if one thinks about it the material balance is the most important description of the plant performance. For instance for a CTL plant, one would want as much of the feed material (carbon in the coal) to appear as product. Any carbon in the feed that does not report to the product is essentially discharged as carbon dioxide into the atmosphere which is very undesirable from both an economic and environmental point of view. The relative amount of carbon that reports to either the product or CO_2 would be described by the overall material balance for the process.

In particular in this paper it will be examined how different decisions one makes affect the material balance and thus the overall efficiency of the process. In principle the three constraints should all be satisfied simultaneously and thus the energy balance and the work (entropy) balance both influence the material balance. This point should become clearer as examples are done below. In order to explain the thinking, each of the constraints will be applied one by one and the impact of the constraints on the process and what it means in terms of synthesising the process will be examined.