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Biodiesel Processes Energy Improvement based on Pinch and Exergy Analysis

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With the growth of energy demands and depleting fossil fuel reserves, there is an increasing incentive to improve an energy efficiency of industrial processes. This project aims to develop energy improvement methodologies containing both Pinch and exergy Analysis in an iterative manner, and identify promising modifications that can be applied on industrial scale processes to improve process energy performance across three criteria: heat recovery, exergetic efficiency, and economic profitability. In this work, the barley straw as the biomass stock feed to produce biodiesel production processes are optimized by Heat Integration to construct heat exchanger network (HEN), and the promising modifications proposed from the results of the exergy analysis are then investigated to reduce the exergy loss of processes. For this case, modifications such as increasing the reaction temperature and adjusting the reactants ratio on the identified three exergetic losses units would reduce the process exergy loss by 23 % and increase the exergetic efficiency by 4.74 %.

1. Introduction

The majority of the current global energy demand is fulfilled by conventional energy resources such as petroleum and coal. As the global energy demand continues to grow up, attention has been paid on developing alternative renewable energy resources that would accommodate the energy demand of the future (Demirbas, 2007). Biomass has great potential as a renewable and clean feed for producing modern energy carriers. Biodiesel has the additional benefit that it is more environmentally friendly with lower emissions than conventional petroleum derived fuels. The agricultural, animal and industrial organic wastes might be biomass feedstock in biomass to biodiesel processes (Ptasinski, 2016).

To enhance the economic profitability of the biodiesel production, it is important to improve the energy efficiency of the processes by maximizing heat recovery and minimizing energy degradation.

There are two methods commonly used for the process energy optimization: pinch and exergy analysis. Both methodologies can be applied on industrial scale processes to improve the energy efficiency of the processes (Thasai and Siemanond, 2015). Pinch Analysis minimizes the energy consumption by identifying the optimal heat exchanger network (HEN) to recover heat within the processes (Klemeš, 2013). It is often used for process integration which usually is a critical step in the process design to minimize the utility costs by maximizing the heat recovery. However, Heat Integration does not necessarily lead to an increase of the exergetic efficiency of the processes.

Exergy analysis is used to identify the most inefficient units in the processes (Mabrouk et al. 2016). If the reasons of exergy degradation on these inefficient units can be explored, the modifications could be presented to increase the exergetic efficiency and decrease the exergy loss. Although exergy analysis allows for the comparison of alternative process structures, it could not not lead to a single optimal solution (Radgenand Lucas, 1996).

This project integrates the Pinch and exergy Analysis to optimize the energy performance of processes.

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2. Methodology development and exergy analysis

2.1 Exergy analysis

Exergy analysis is extensively used in industry to identify areas of thermodynamic inefficiencies (Kotas, 1995). Exergy, *Ex*, is contributed by three components: chemical exergy Ex_{che}, physical exergy Ex_{phy}, and the exergy changes due to mixing. The last one is usually negligible in the exergy calculation.
The exergy, *Ex*, is calculated based on the Szargut model (Szargut, 2005), following the Eqs(1-3):

$$Ex = Ex_{phy} + Ex_{che} \tag{1}$$

$$Ex_{phy} = m\left[\left(h - h_0\right) - T_0\left(s - s_0\right)\right] \tag{2}$$

$$Ex_{che} = m\left[\sum_i x_i Ex_{0,i} + RT_0 \sum_i x_i Inx_i\right] \tag{3}$$

Exergy analysis involves performing an exergy balance over the processes to determine the exergy losses and exergetic efficiency (Modarresi et al., 2010). Exergy loss *I* in Equation (4) is the result of irreversible degradation of the thermodynamics. The exergetic efficiency η in Equation (5) is a ratio of the exergy of the outlet to the inlet streams if the exergy destruction is assumed as the only form of the exergy loss.
To achieve the maximum exergetic efficiency, the thermodynamic driving forces of the processes should be the minimum.

$$I = Ex_{in} - Ex_{out} \tag{4}$$

$$\eta = \frac{Ex_{out}}{Ex_{in}} \tag{5}$$

2.2 Potential process improvements based on exergy analysis

Industrial applications of exergy efficiency and exergy loss analysis are investigated to identify the thermodynamic shortcomings of the processes.
Heuristics and rigorous thermodynamic analysis are important approaches for proposing modifications to processes units to reduce the thermal deduction and increase the exergetic efficiency of the inefficient units.
General heuristics applied to maximize the exergetic efficiency of the whole processes is firstly looked at.
For instance, distillation column is the most commonly used separator. Based on 'the principle of equipartition of entropy production' developed by Tondeur and Kvaalen (1987), the aim of the modifications should be evening out the driving force distribution. Therefore, feed conditioning, feed splitting, feed stage location, the reflux ratio, and adding side condensers or reboilers are considerations to be adjusted to improve the exergetic efficiency (Zemp, et al., 1997).
The similar principle can be applied in the heat exchanger exergy analysis. Reducing the thermodynamic driving forces can reach high exergetic efficiency. Thus, a counter-current heat exchanger would be more exergetically efficient than a co-current exchanger because of more evenly distributed temperature difference across the unit. Note, there exists a trade-off between the lower driving force which is beneficial for higher exergetic efficiency and the larger heat transfer area as the cost. It illustrates that the exergy analysis is not the only criteria to improve the processes energy performance.
For chemical reactors, the general heuristics are operating exothermic reactions at higher temperatures and operating endothermic reactions at lower temperatures. Still, these heuristics might be limited by reaction kinetics (Ptasinski, 2016). For example, a combustion chamber as an exothermic reaction at higher temperature is more effective in exergy than lower temperature. But, the chamber construction and NOx formation limits the highest combustion temperature (Tsatsaronis and Cziesla, 2004).
Again, exergetic efficiency is not the only criteria of the process modifications. Other criteria such as economics and operability should also be considered.

2.3 Improvement iteration

The methodology to be undertaken to improve the energy efficiency of the processes is proposed in Figure 1. The integrated processes with HEN subjected to feasibility and operability constraints are firstly explored, and then the most inefficient units are identified. Process modifications are presented to reduce the process exergy loss. This is an iteration optimization.

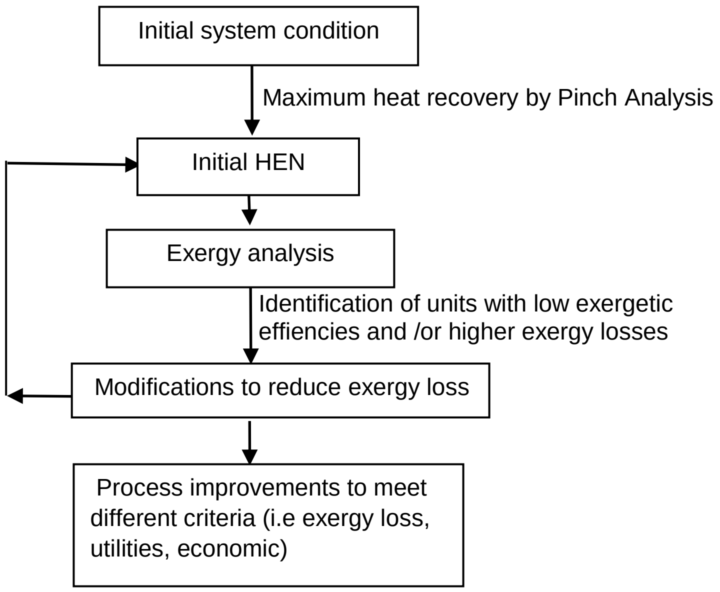

Figure 1: The iteration methodology for process improvement by Pinch and Exergy analysis

3. Case study

Barley straw to transportation liquid processes consist of the following units: biomass pyrolysis, gasification, water gas shift, acid gas removal, CO_2 capture, Fischer-Tropsch (FT) synthesis, syncrude refining and tail gas treating by reforming reaction (Sun et al., 2015). The barley straw feed is 100 t·h^{-1}. Table 1 lists the operating conditions of main units.

Table 1: Operating conditions in the barley straw *into biodiesel processes*

Unit	Operational Conditions
Pyrolysis(PYRO)	T = 450 °C, P = 2 bar
Gasiification (C-GAS)	T = 500 °C, P = 2 bar
Combustion reaction-1 (COMB1)	T = 1,400 °C, P = 14 bar
Bio oil Gasiification-1 (GAS-1)	T = 500 °C, P = 2 bar
Bio oil Gasiification-2 (GAS-2)	T = 1,050 °C, P = 30 bar
Shift-1 (WGS)	T= 500 °C, P= 2 bar
Shift-2 (WGS)	T= 450 °C, P= 4 bar
Absorption	T= 500 °C, P= 2 bar
Multi- compression (MCOM)	P_{out} = 80bar
Fischer-Tropsch (FT)	T= 200 °C, P = 25 bar
Flash (FLASH)	T= -35 °C, P = 1 bar
Catalytic cracking (HCRAC)	T= 360 °C, P = 45 bar
Combustion reaction -2(COMB2)	T= 1,400 °C, P = 25 bar
Reforming reaction (REFO)	T= 1,000 °C, P = 30 bar

The initial HEN is designed based on the Pinch Analysis to achieve the maximum heat recovery with the assumption of ΔT_{min} = 5 °C.

Table 2 lists the exergy loss and exergetic effic of heat exchngers in the Pinch based HEN. There are 12 heat exchangers in the HEN. Most of exchangers have high exergetic efficiencies (>90%) except H7-H9. The exergy losses lying in these three exchangers are very lower compared with other three exchangers H5, H6 and H12, which contributed 84.2 % of the overall exergetic losses in the heat exchanger network. Measures should be taken to reduce the losses of these exchangers. For the H5, the syngas from the gasifier at 1400 °C should be recovered by HP and MP steam generation and process heating in sequence instead of process heating directly as the hot stream in the initial HEN. Excessive temperature difference is the main reason to cause the large values of exergy loss for both H6 and H12. Increasing heat transfer area heat by adding new exchangers could greatly lower down the temperature difference and the exergy loss.

Table 2: Exergy Analysis of heat exchangers

Heat exchanger	Exergy loss, kW	Exergetic efficiency, %	Heat exchanger	Exergy loss, kW	Exergetic efficiency, %
H1	14.7	98.4	H7	41.1	78.0
H2	57.6	96.2	H8	25.9	75.5
H3	6.8	98.4	H9	123.7	83.6
H4	15.6	96.0	H10	34.6	90.8
H5	898.7	96.4	H11	12.3	93.5
H6	510.9	98.3	H12	361.9	90.8

The comparisons between the Pinch based HEN and the improved HEN using both Pinch and exergy analysis are listed in Table 3. Even though the heat transfer area of the improved HEN is larger than that of the initial HEN, both hot and cold utility demands for the improved HEN decrease 124.5 kW and 124.9 kW separately to save the total cost \$ 88.7 $\times 10^3$ every year.

Table 3: Comparisons between the initial HEN and the improved HEN

	Pinch based HEN	Improved HEN
Exchanger areas, m^2	5,829.6	5,991.1
Cold utility, kW	2,423	2,298
Hot utility, kW	2,799	2,674
Capital cost, $\times 10^3$ \$/y	484.5	497.9
Operating cost, $\times 10^3$ \$/a	2,160.6	2,058.5
Total cost, $\times 10^3$ \$/a	2,545.1	2,556.4

Exergy analysis of key units in the processes are listed in Table 4. The exergy of the barley is calculated based on following Equations (Szargut, 2005):

$$Ex_{straw} = \beta_{straw} m_{straw} LHV_{straw} \tag{6}$$

$$\beta_{straw} = \frac{1.044 + 0.016\frac{[H]}{[C]} - 0.3493\frac{[O]}{[C]}\left(1 + 0.0531\frac{[H]}{[C]}\right) + 0.0493\frac{[N]}{[H]}}{1 - 0.4124\frac{[O]}{[C]}} \tag{7}$$

$$LHV_{straw} = HHV_{straw} - 21.978[H] \tag{8}$$

$$HHV_{straw} = 0.3491[C] + 1.1783[H] + 0.0151[N] - 0.1034[O] - 0.0211[A] \tag{9}$$

Table 4: Exergy analysis of the units in the in the barley straw *into biodiesel processes*

Unit	Exergy loss, kW	Exergetic efficiency, %	Unit	Exergy loss, kW	Exergetic efficiency, %
PYRO	9,307	92.52	WGS-2	1,065	97.85
C-GAS	5,013	79.13	ABSOR	6,700	91.53
COMB1	5,397	85.63	HCRAC	11615	83.62
GAS-1	12,693	83.57	MCOM	13	99.81
GAS-2	19,911	71.21	FT	40,863	56.43
WGS-1	6,295	88.98	FLASH	8,881	83.22
COMB2	4,847	81.92	REFO	29,363	57.57

From the above Table, the total exergy loss of the process is 164.9×10^3 kW, and the process exergetic efficiency is 81.46 %. There are three units operating at lower exergetic efficiencies: FT, REFO and GAS-2. The exergy loss from these three units contributes 54.66% of the overall exergy loss.

The following measures are presented to reduce the exergy loss in these three units.

1) Raising the operating Temperature in the FT

FT temperature is one of the key operating parameters to affect the products distribution greatly. Higher FT temperature is beneficial for the conversion of the heavy hydrocarbon, which has higher specific heat capacity and higher standard chemical exergy than light hydrocarbon. In this case, raising the FT temperature to be 220 °C from 200 °C can improve the exergetic efficiency from 56.43 % to 70.69 %.

2) Increasing the molar ratio of O_2 to FT tail gas (O_2/FT-TG) in the REFO

The ratio of O_2 to FT-TG is 0.12 in the base case. Based on the sensitivity analysis, the optimal ratio of O_2 to FT-TG is 0.18 to achieve the maximum conversion ratio of the syngas. The exergetic efficiency increases 14.58 % to be 72.15 % at the optimal ratio of O_2 to FT-TG.

3) Reducing Oxygen equivalent ratio (ER) in GAS-2

In the base case, excess oxygen reacting with the syngas at ER = 0.28 reduces both the syngas heat value and the exergetic efficiency. Figure 2 illustrate the relationship between the ER and the exergetic efficiency of the gasifier. ER falls to be 0.20 can increase the exergetic efficiency to be 85.62 % .

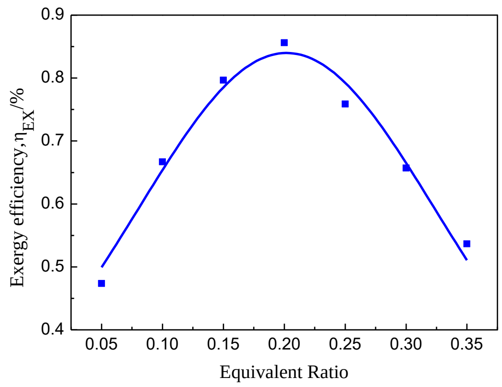

Figure 2: Sensitivity analysis of equivalent ratio on exergetic efficiency in the gasifier

The exergy loss and exergetic efficiency of the processes with above operating modifications are compared with the initial processes in Table 5. The exergetic efficiency increases 4.74%, and exergy loss reduces by 23%, that is, 38.827 $\times 10^3$ kW exergy loss saving of the whole processes.

Table 5: Exergy analysis for the production processes

	Initial processes	Improved processes
Exergy loss, $\times 10^3$ kW	164.902	126.074
Exergetic efficiency, %	81.46	86.20

4. Conclusions

The Iterative Pinch and exergy Analysis can be applied in both new processes design and retrofitting of existing processes to improve the energy efficiency and reduce exergy losses simultaneously.

The proposed method has been applied in the barley straw into biodiesel processes. Based on the analysis on utility demands and the exergy loss distribution of the processes, the reforming reaction (REFO), the 2nd gasifier (GAS-2), and FT reactor (FT) are the top three exergetic losses units, which contribute 54.66 % of the total exergy losses of the processes. The proposed modifications on these three units improve the exergetic efficiency of the processes from 81.46% to be 86.20 %, and reduce the exergy loss by 38.827 $\times 10^3$ kW, via increasing the operating temperature in the FT, Increasing the molar ratio of O_2 to FT tail gas in the REFO, and decreasing Oxygen equivalent ratio in the GAS-2. The exergy analysis can improve process energy utilization by reducing the quality of energy streams in the process is not degraded.

This methodology provides alternative measures other than the conventional economic analysis. However, it should be noted the proposed improvements for exergy analysis might need more capital or operating cost. The results obtained for the exergy analysis is independent of other factors such as economic performance, the unit operability, and the process sustainability. The methodology may have to be further developed to be more established and comparable to economic and operability analysis.

Nomenclatures

$Ex_{che:}$ chemical exergy, kW
$Ex_{phy:}$ physical exergy, kW
$Ex_{in:}$ inlet exergy, kW
Ex_{out}: outlet exergy, kW
Ex_o: standard chemical exergy, kW
h: specific enthalpy, kJ/kg
HHV: High heat value, kJ/kg
i: the unit, including heat exchanger, reactor, and absorption column.
I: exergy loss, kW
LHV: low heat value, kJ/kg
m: mass rate, kg/s
o: baseline state (T_0 = 298.15 K, P = 101.33 kPa)
s: specific entropy, kJ/ kg/K
x_i: mass fraction of the component *i*
β: correlation factor
[A]: Ash mass fraction
[H], [C], [O], [N]: mass fraction of H, C, O, and N

References

Demirbas A., 2007, Importance of Biodiesel as Transportation Fuel, Energy Policy, 35(9), 4661– 4670.

Klemeš J.J. (Ed), 2013, Handbook of Process Integration (PI): Minimisation of Energy and Water Use, Waste and Emissions, Woodhead/Elsevier, Cambridge, UK.

Kotas T., 1995, Solutions Manual To Accompany the Exergy Method of Thermal Plant Analysis, Malabar: Krieger.

Mabrouk A., Erdocia X., González-Alriols M., Labidi J., 2016, Assessment of the Exergy Performance of an Organosolv Process using Aspen Plus®, Chemical Engineering Transactions, 52, 85 – 90.

Modarresi A., Wukovits W., Foglia D., Friedl, A., 2010, Effect of Process Integration on the Exergy Balance of a Two-Stage Process for Fermentative Hydrogen Production, Journal of Cleaner Production, 18, 63 – 71.

Prins MJ., Ptasinski K.J., Janssen F.J.J.G., 2007, From Coal to Biomass Gasification: Comparison of Thermodynamic Efficiency, Energy, 32(7), 248 – 1259.

Ptasinski, K., 2016, Efficiency of Biomass Energy: An Exergy Approach to Biofuels, Power, and Biorefineries, John Wiley & Sons.

Radgen P., Lucas K., 1996, Energy system analysis is fertilizer complex - Pinch Analysis vs. Exergy analysis, Chemical Engineering & Technology, 19(2), 192 – 195.

Sun L., Xu B., Smith R., Study of Tail Gas Treatment in Barley Straw Gasification Processes Integration with Utility Systems, 2015, Energy Procedia, 75, 2351 – 2356.

Szargut J., 2005, Exergy methed:techmical and ecological applications[, Boston:WTT Press,Southampton.

Thasai J., Siemanond K., 2015, Combined Exergy-Pinch Analysis to Improve Cryogenic Process, Chemical Engineering Transactions, 43, 1435 – 1440.

Tondeur D., Kvaalen E., 1987, Equipartition of Entropy Production. An Optimality Criterion for Transfer and Separation Processes, Industrial & Engineering Chemistry Research, 26(1), 50 – 56.

Tsatsaronis G., Cziesla F., 2004, Exergy Analysis of Simple Processes. Exergy, Energy System Analysis and Optimization, vol 1, EOLSS Publishers, Oxford, 79 – 107.

Zemp R.J., De Faria S.H.B., Olievira Maia M.D.L., 1997, Driving Force Distribution and Exergy Loss in the Thermodynamic Analysis of Distillation Columns, Computers & Chemical Engineering, 21, 523 – 528.