

The Potential of Liquefied Oxygen Storage for Flexible Oxygen-Pressure Swing Adsorption Unit

Radek Šulc*, Pavel Ditl

Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Process Engineering, Technická 4, Prague, Czech Republic
 Radek.Sulc@fs.cvut.cz

The pressure swing adsorption (PSA) units are widely used as an oxygen source. Start-up time taking minutes is an undeniable advantage of PSA technology compared to cryogenic air separation start-up time taking hours or days. The increasing share of renewable electricity causes intraday electricity price fluctuations. These fluctuations can be an opportunity to improve the economy of a plant and/or to accumulate electricity in the form of liquefied products. This paper aims to demonstrate the possibility of a flexible PSA unit connected to a small oxy-fuel combustion unit. Two options were analyzed: i) LOX supply at electricity price peak, and ii) liquid oxygen energy storage (LOES). The cold energy needed for oxygen liquefaction will be obtained utilizing liquefied nitrogen (LIN) delivered from a large air separation unit (ASU). The analysis was carried out for the Czech Republic, the Federal Republic of Germany, and the Kingdom of Denmark. These countries differ significantly in the energy mix.

1. Introduction

The Pressure Swing Adsorption (PSA) units are widely used as oxygen sources where oxygen is produced in gaseous form. Start-up time taking minutes is an undeniable advantage of PSA technology compared to cryogenic air separation start-up time taking hours or days. The capacity of a pressure vessel limits the storage of pressurized gaseous oxygen.

The increasing share of renewable electricity causes intraday electricity price fluctuations. These fluctuations can be an opportunity to improve the economy of a plant (Miller et al., 2008) depending on market conditions (Cao et al., 2017), and to accumulate electricity in the form of liquefied products (Caspero et al., 2019a, 2019b). Miller et al. (2008) analyzed the energy and capital costs of a cryogenic air separation unit (ASU). They proposed a simplified economic model enabling to take hourly variations in electricity prices into account. Cao et al. (2017) presented a dynamic model for pre-emptive ASU performance prediction depending on market conditions. Casperi et al. (2019a) designed a flexible ASU with an integrated liquefaction cycle and liquid assist operation. This ASU allows changing the power demand from 3.5 to 28 MW without violating operational constraints by changing the nitrogen and oxygen production. The flexibility of the designed process was tested over a time horizon of two days with historical electricity prices, and an improvement of 14 % was found in comparison with quasi-stationary scheduling (Caspero et al., 2019b). This way, the energy can be stored in the form of a cold energy storage system. Liu et al. (2020) studied the applicability of single- and multi-component fluid cycles for liquid air energy storage (LAES) to increase the performance of cold cycles for air liquefaction.

The increasing number of sizeable cryogenic air separation units connected to oxy-combustion power plants or integrated gasification combined cycle plants can generate large amounts of nitrogen whose utilization is limited but can be utilized for energy storage in the liquid form.

This paper aims to demonstrate the possibility of a flexible PSA unit connected to a small oxy-fuel combustion unit. The following two options were analyzed: i) LOX supply in the electricity peak, and ii) the liquid oxygen energy storage (LOES) where the cold energy needed for oxygen liquefaction will be obtained utilizing liquefied nitrogen (LIN) delivered from a large ASU unit.

2. Oxygen production by Pressure Swing Adsorption

Šulc and Ditl (2021b) investigated the potential of consumed energy savings in the PSA unit used as an oxygen source for the oxy-fuel combustion unit to reach the ecologically friendlier processing. They analyzed the following four options: i) single or dual compression, ii) utilization of waste compression heat for coal or biomass dewatering, iii) utilization of dry waste gas from the PSA unit for coal or biomass dewatering, and iv) energy recovery by an expansion of pressurized oxygen (GOX) before combustion. The analysis was carried out for on-site oxygen production using two-bed Pressure Swing Adsorption for 95 % purity and oxygen recovery characterized by the air ratio of $10 \text{ Nm}^3 \text{ Nm}^{-3}$ producing $101 \text{ Nm}^3 \text{ h}^{-1}$ of gaseous oxygen (GOX). They identified the highest potential of energy saving for dual compression and utilization of low-grade waste compression heat for fuel drying. 10 % of the electrical energy may be saved, and the specific energy consumption decreases from $0.805 \text{ kWh kg}_{\text{O}_2}^{-1}$ for a single compression to $0.728 \text{ kWh kg}_{\text{O}_2}^{-1}$ using dual compression. It represents a saving of 85.68 MWh y^{-1} for the annual operating time of 8,160 h. Utilization of low-grade waste compression heat for fuel drying was enabled to reduce fuel consumption depending on fuel moisture, e.g., by 5.3 % or 10.4 % of lignite or wood, respectively, for reference fuel conditions. The data mentioned above were obtained for ambient air and compressed air at an outlet temperature of $30 \text{ }^\circ\text{C}$ and outlet pressure of 750 kPa (a) at the PSA unit inlet. The pressure losses of inter-and after-coolers were taken into account.

3. Intra-day electricity prices

The electricity cost is a major cost item of oxygen production by pressure swing adsorption. Electricity prices vary from country to country, from supplier to supplier, and depend considerably on annual electricity take-off (Šulc and Ditl, 2021a). For the analysis, the day-ahead prices reported by ENTSO-E Transparency Platform were used. No taxes (VAT and recoverable taxes) and levies were not taken into account. The prices vary during the year, months, and days. Therefore, the data for the randomly selected 2nd Wednesday in January, April, July, and October of the year 2020 respecting the winter, spring, summer, and autumn seasons, respectively, were overtaken. The analysis was carried out for the Czech Republic, the Federal Republic of Germany, and the Kingdom of Denmark. These countries differ significantly in the energy mix. The Czech Republic generated an average approx. 36 % in nuclear power plants, 49 % in thermal power plants, and 14 % by renewable energy sources in selected days (Figure 1 in detail). Unlike this, Denmark generated an average of approx. 25 % of energy in thermal power plants, 75 % renewable energy sources, and no energy is produced in nuclear power plants. The energy mix of Germany was between both countries. Germany generated an average approx. 12 % of energy in nuclear power plants, 40 % in thermal power plants, and 47 % renewable energy sources.

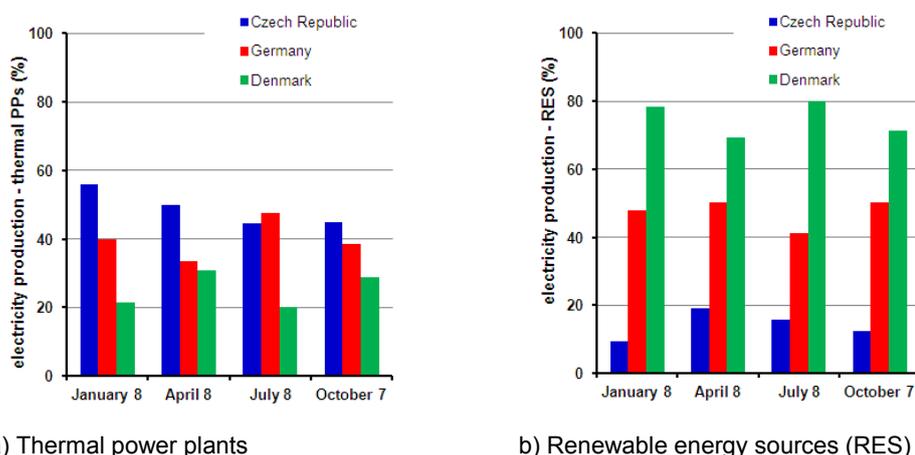


Figure 1: Share of sources for electricity production: a) thermal power plants (coal, gas, waste combustion), b) renewable energy sources (solar, wind, biomass, water)

The day-ahead prices for January 8, April 8, July 8, and October 7 of the year 2020 and their comparison for the Czech Republic, Germany, and Denmark are presented in Figure 2. The significant morning and evening peaks are visible from 7 to 12 a.m. and from 7 to 9 p.m. In some cases, a significant price falls due to an excess of renewable energy sources.

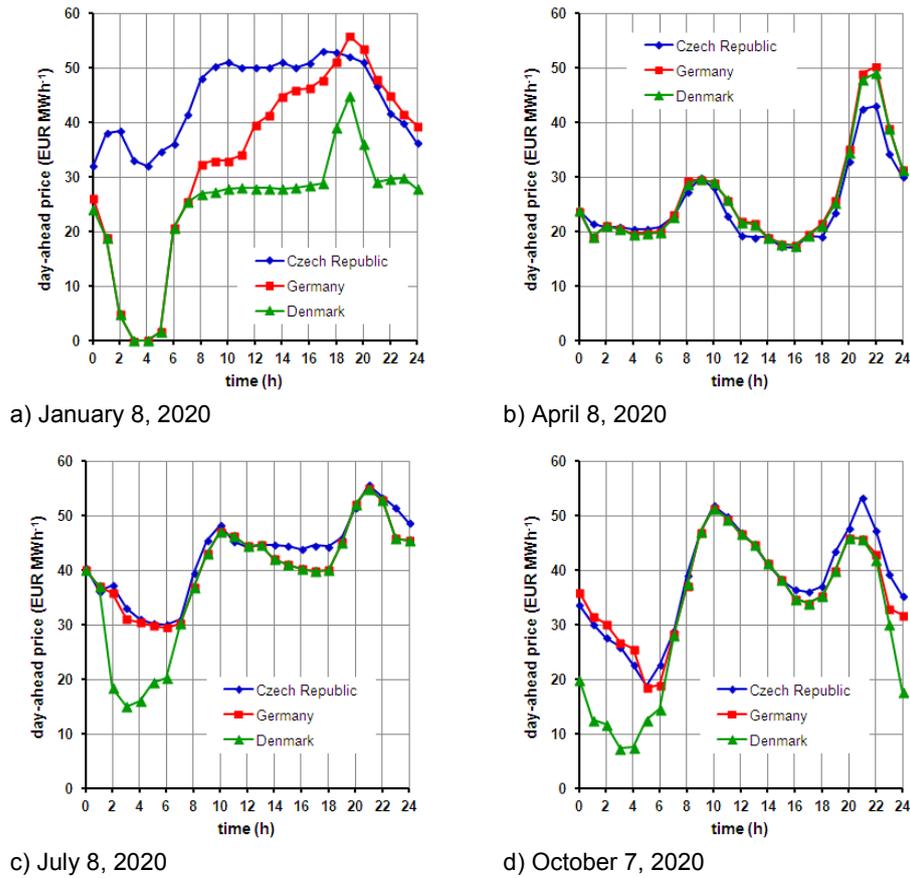


Figure 2: Day-ahead prices for the Czech Republic, Germany, and Denmark: a) January 8, 2020; b) April 8, 2020; c) July 8, 2020; d) October 7, 2020

4. LOX supply at electricity price peak

The benchmark specific electricity consumption of liquefied oxygen (LOX) is $638 \text{ kWh t}_{\text{LOX}}^{-1}$ (EIGA, 2019). The difference between the specific electricity consumption of LOX and GOX produced by the PSA unit may be utilized for cost-saving. In this case, the oxygen needed for the process is supplied by the PSA unit during a period in which the electricity price is low. During the electricity price peak, the oxygen needed for the process is produced from liquefied oxygen (LOX) supplied from large ASU facilities continuously operated through a day. Liquefied oxygen is evaporated by ambient air.

The following assumptions were adopted for the following model for calculating the cost-saving:

- 1) the electricity cost is taken only into account; the investment cost and other operational costs such as depreciation, maintenance, etc. are not included,
- 2) the LOX price is estimated based on the benchmark specific electricity consumption of LOX production and the daily averaged day-ahead electricity price,
- 3) the LOX transportation cost is not included.

The daily average electricity price $c_{\text{el-daily}}$ (EUR MWh⁻¹) was obtained numerically by the trapezoidal integration method. The off-peak average electricity price $c_{\text{el-offpeak}}$ (EUR MWh⁻¹) was calculated analogically by the same procedure but for the off-peak period. The 24-hour operation and peak periods from 7 a.m. to 12 a.m. and from 6 p.m. to 9 p.m. were assumed. The electricity cost $C_{\text{el-PSA-daily}}$ (EUR d⁻¹) for PSA unit operated for an operation time Δt_{oper} (h) was calculated:

$$C_{\text{el-PSA-daily}} = c_{\text{el-daily}} \cdot e_{\text{PSA}} \cdot \Delta t_{\text{oper}}, \quad (1)$$

where e_{PSA} (MWh t_{O₂}⁻¹) is the specific electricity consumption of the PSA unit. The electricity cost $C_{\text{el-PSA-off-peak}}$ (EUR d⁻¹) for PSA unit operated during off-peak period $\Delta t_{\text{off-peak}}$ (h) was calculated:

$$C_{\text{el-PSA-off-peak}} = c_{\text{el-off-peak}} \cdot e_{\text{PSA}} \cdot \Delta t_{\text{off-peak}}. \quad (2)$$

The LOX cost $C_{\text{LOX-peak}}$ (EUR d⁻¹) for LOX consumed during peak period Δt_{peak} (h) was calculated:

$$C_{\text{el-LOX-peak}} = C_{\text{el-daily}} \cdot e_{\text{LOX}} \cdot \Delta t_{\text{peak}} = C_{\text{el-daily}} \cdot e_{\text{LOX}} \cdot (\Delta t_{\text{oper}} - \Delta t_{\text{off-peak}}), \quad (3)$$

where e_{LOX} (MWh t_{LOX}⁻¹) is the specific electricity consumption of LOX production. Then, the cost saving is estimated as it follows:

$$\text{cost-saving (\%)} = 100 \cdot (C_{\text{el-PSA-off-peak}} + C_{\text{el-LOX-peak}}) / C_{\text{el-PSA-daily}}. \quad (4)$$

The cost-saving calculated using the proposed model is presented in Tables 1, 2, and 3 for the Czech Republic, Germany, and Denmark.

Table 1: LOX supply at electricity price peak – the Czech Republic

Description	Unit	January 8	April 8	July 8	October 7
<i>Input data</i>					
Daily average day-ahead price ^{*1}	EUR MWh ⁻¹	44.84	24.54	42.59	38.00
Off-peak average electricity price ^{*1}	EUR MWh ⁻¹	42.40	23.30	41.15	34.34
LOX price based on daily average el. price ^{*1,2}	EUR t _{O₂} ⁻¹	28.61	15.66	27.17	24.24
<i>Single compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	866	474	823	734
PSA unit: cost for off-peak production	EUR d ⁻¹	546	300	530	442
LOX consumed during electricity price peaks	EUR d ⁻¹	229	125	227	194
Oxygen cost by combined PSA+LOX	EUR d ⁻¹	775	425	747	636
Cost saving ^{*5}	%	10.5	10.3	9.2	13.3
<i>Dual compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	784	429	744	664
PSA unit: cost for off-peak production	EUR d ⁻¹	494	271	479	400
LOX consumed during electricity price peaks	EUR d ⁻¹	229	125	217	194
Oxygen cost by combined PSA+LOX	EUR d ⁻¹	723	397	697	594
Cost saving ^{*5}	%	7.8	7.5	6.4	10.5

Note: ^{*1} Operation time = 24 h d⁻¹, peak period: from 7 a.m. to 12 a.m. and from 6 p.m. to 9 p.m.

Note: ^{*2} Specific electricity demand for LOX production: 0.638 MWh t_{O₂}⁻¹.

Note: ^{*3} PSA unit: ambient air: temperature of 20 °C, pressure of 100 kPa (a), relative humidity of 70 %; compressed air; outlet temperature of 30 °C, outlet pressure of 750 kPa (a); specific electricity demand: single compression 0.805 MWh t_{O₂}⁻¹, dual compression 0.728 MWh t_{O₂}⁻¹.

Note: ^{*4} Calculation was performed for the specific oxygen production capacity of 1 t h⁻¹.

Note: ^{*5} Cost savings: related to the cost of PSA production for daily average electricity price.

Table 2: LOX supply at electricity price peak – Germany

Description	Unit	January 8	April 8	July 8	October 7
<i>Input data</i>					
Daily average day-ahead price ^{*1}	EUR MWh ⁻¹	33.31	26.01	40.99	36.82
Off-peak average electricity price ^{*1}	EUR MWh ⁻¹	29.67	24.44	39.28	33.37
LOX price based on daily average el. price ^{*1,2}	EUR t _{O₂} ⁻¹	21.25	16.59	26.15	23.49
<i>Single compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	644	502	792	711
PSA unit: cost for off-peak production	EUR d ⁻¹	382	315	506	430
LOX consumed during electricity price peaks	EUR d ⁻¹	170	133	209	188
Oxygen cost by combined PSA+LOX	EUR d ⁻¹	552	448	715	618
Cost saving ^{*5}	%	14.2	10.9	9.7	13.1
<i>Dual compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	582	454	716	643
PSA unit: cost for off-peak production	EUR d ⁻¹	346	285	457	389
LOX consumed during electricity price peaks	EUR d ⁻¹	170	133	201	188
Oxygen cost by combined PSA+LOX	EUR d ⁻¹	516	417	667	577
Cost saving ^{*5}	%	11.4	8.1	6.9	10.3

Note: ^{*1-5} see Table 1 in detail.

Table 3: LOX supply at electricity price peak – Denmark

Description	Unit	January 8	April 8	July 8	October 7
<i>Input data</i>					
Daily average day-ahead price ^{*1}	EUR MWh ⁻¹	24.44	25.72	38.17	32.50
Off-peak average electricity price ^{*1}	EUR MWh ⁻¹	20.91	24.20	35.05	26.87
LOX price based on daily average el. price ^{*1,2}	EUR tO ₂ ⁻¹	15.59	16.41	24.35	20.73
<i>Single compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	472	497	737	628
PSA unit: cost for off-peak production	EUR d ⁻¹	269	312	451	346
LOX consumed during electricity price peaks	EUR d ⁻¹	125	131	195	166
Oxygen cost by combined PSA+LOX	EUR	394	443	646	512
Cost saving ^{*5}	%	16.6	10.8	12.4	18.5
<i>Dual compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	427	449	667	568
PSA unit: cost for off-peak production	EUR d ⁻¹	244	282	408	313
LOX consumed during electricity price peaks	EUR d ⁻¹	125	131	195	166
Oxygen cost by combined PSA+LOX	EUR d ⁻¹	368	413	603	479
Cost saving ^{*5}	%	13.8	8.0	9.6	15.7

Note:^{*1-5} see Table 1 in detail.

Table 4: On-site oxygen liquefaction and liquid oxygen energy storage (LOES) – Denmark

Description	Unit	January 8	April 8	July 8	October 7
<i>Input data</i>					
Daily average day-ahead price ^{*1}	EUR MWh ⁻¹	24.44	25.72	38.17	32.50
Average electricity price for storage period ^{*1}	EUR MWh ⁻¹	5.35	20.07	19.52	10.66
LIN price based on daily average el. price ^{*1,2}	EUR tN ₂ ⁻¹	13.42	14.12	20.95	17.84
<i>Single compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	472	497	737	628
PSA unit: cost for off-peak production	EUR d ⁻¹	429	439	675	555
PSA unit: cost for stored production (LOES)	EUR d ⁻¹	22	81	79	43
LIN consumed for liquefaction (LOES) ^{*5}	EUR d ⁻¹	63	66	98	83
Oxygen cost by combined PSA+LOES	EUR d ⁻¹	514	586	851	682
Gain (+)/loss (-) ^{*6}	%	-8.8	-17.9	-15.5	-8.6
<i>Dual compression ^{*3,4}</i>					
PSA unit: cost for daily average el. price	EUR d ⁻¹	427	449	667	568
PSA unit: cost for off-peak production	EUR d ⁻¹	313	320	491	404
PSA unit: cost for stored production (LOES)	EUR d ⁻¹	19	73	71	39
LIN consumed for liquefaction (LOES) ^{*5}	EUR d ⁻¹	63	66	98	83
Oxygen cost by combined PSA+LOES	EUR d ⁻¹	395	459	660	526
Gain (+)/loss (-) ^{*6}	%	7.6	-2.1	1.0	7.3

Note:^{*1} Operation time = 24 h d⁻¹, storage period from 1 a.m. to 6 a.m., peak period: from 8 a.m. to 10 a.m. and from 7 p.m. to 10 p.m.

Note:^{*2} Specific electricity demand for LIN production: 0.549 MWh tN₂⁻¹.

Note:^{*3} see Table 1 in detail.

Note:^{*4} Calculation was performed for the specific oxygen production capacity of 1 t h⁻¹.

Note:^{*5} Specific LIN consumption for oxygen liquefaction: 0.935 kg_{LIN} kgO₂⁻¹.

Note:^{*6} Gain/loss: related to the cost of PSA production for daily average electricity price.

5. On-site oxygen liquefaction and liquid oxygen energy storage (LOES)

When the electricity price is lowest, the second PSA unit is started, and the on-site produced gaseous oxygen is liquefied and stored in the storage tank. The cold energy needed for oxygen liquefaction will be obtained utilizing liquefied nitrogen (LIN) delivered from large ASU facilities continuously operated throughout the day. During the electricity price peak, the stored liquefied oxygen produced during the storage period is regasified and supplied to the consumer technology, e.g., in the oxyfuel combustion unit. Outside the electricity price peak, the oxygen needed is provided by the master PSA unit. The required second PSA unit, which is not fully exploited during the day, may seem to be a disadvantage of this solution. However, the critical pieces of

equipment in the industry are usually doubled to ensure the reliability of the plant operation. The assumptions analogical to the previous option were adopted for calculating the effectiveness of the process proposed. The 24 h operation storage period from 1 a.m. to 6 a.m., and peak periods from 8 a.m. to 10 a.m. and from 7 p.m. to 10 p.m. were assumed. Assuming the liquefaction of gaseous oxygen (95 % O₂, 5 % Ar) at 400 kPa by LIN evaporated at the pressure of 101 kPa, the specific LIN consumption of 0.935 kg_{LIN} kg_{O₂}⁻¹ was calculated using ASPEN+ software. The LIN cost C_{LIN-storage} (EUR d⁻¹) for LIN consumed for oxygen liquefaction during the storage period Δt_{storage} (h) was calculated:

$$C_{\text{el-LIN-storage}} = C_{\text{el-daily}} \cdot e_{\text{LIN}} \cdot \Delta t_{\text{storage}}, \quad (5)$$

where e_{LIN} (MWh t_{LIN}⁻¹) is the specific electricity consumption of LIN production. The benchmark specific electricity consumption of liquefied nitrogen (LIN) is 549 kWh t_{LIN}⁻¹ (EIGA, 2019).

Then, the gain(+)/loss(-) rate is estimated as it follows:

$$\text{gain/loss (\%)} = 100 \cdot (C_{\text{el-PSA-off-peak}} + C_{\text{el-PSA-storage}} + C_{\text{el-LIN-storage}}) / C_{\text{el-PSA-daily}}. \quad (6)$$

The effectiveness of on-site oxygen liquefaction and storage calculated using the proposed model is presented in Table 4 for Denmark only. The positive benefit was found only for the PSA unit with double compression when the electricity price in the storage period was approx. three-four times lower than the daily average electricity price. In the Czech Republic and Germany, the price volatility was insufficient to reach positive effectiveness.

7. Conclusions

This paper aims to demonstrate the possibility of a flexible PSA unit connected to a small oxy-fuel combustion unit. The following two options were analyzed: i) LOX supply in electricity price peak, and ii) liquid oxygen energy storage (LOES). The cold energy needed for oxygen liquefaction will be obtained utilizing liquefied nitrogen (LIN) delivered from a large air separation unit. The theoretical potential of LOX supply in electricity price peak was found to be around 10-14 % of cost-saving compared with the daily operation of PSA unit when the off-peak average electricity price was from 90 to 86 % of the daily average electricity price respectively. Widening the price gap, the potential is growing. Unlike this, the on-site oxygen liquefaction and storage was found to be effective only for PSA units with double compression when the electricity price in the storage period was approx. three-four times lower than the daily average electricity price. Combining the PSA unit and the electricity accumulator seems to be a more prospective technology for more effective on-site oxygen production.

Acknowledgements

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic under OP RDE grant number CZ.02.1.01/0.0/0.0/16_019/0000753 "Research center for low-carbon energy technologies".

References

- Cao Y., Swartz Ch.L.E., Flores-Cerrillo J., 2017, Preemptive dynamic operation of cryogenic air separation units, *AIChE J*, 63, 3845-3859.
- Caspari A., Offermanns Ch., Schäfer P., Mhamdi A., Mitsos, A., 2019a, A flexible air separation process: 1. Design and steady-state optimizations, *AIChE J*, 65, e16705.
- Caspari A., Offermanns Ch., Schäfer P., Mhamdi A., Mitsos A., 2019b, A flexible air separation process: 2. Optimal operation using economic model predictive control, *AIChE J*, 65, e16721.
- Day-ahead prices, resolution PT60M (dataset), ENTSO-E Transparency Platform <transparency.entsoe.eu/dashboard/show> accessed 01.05.2021.
- EIGA, 2019, Indirect CO₂ emissions compensation: Benchmark proposal for Air Separation Plants. Report No. PP 33/19, European Industrial Gases Association (EIGA), Brussels, Belgium.
- Generation per production type (dataset), ENTSO-E Transparency Platform <transparency.entsoe.eu/generation/r2/actualGenerationPerProductionType/show> accessed 01.05.2021.
- Liu Z., Kim D., Gundersen T., 2020, Multi-component fluid cycles in liquid air energy storage, *Chemical Engineering Transactions*, 81, 55-60.
- Miller J., Luyben W.L., Blouin S., 2008, Economic Incentive for Intermittent Operation of Air Separation Plants with Variable Power Costs, *Industrial & Engineering Chemistry Research*, 47, 1132-1139.
- Šulc R., Dítl P., 2021a, A technical and economic evaluation of two different oxygen sources for a small oxy-combustion unit, *Journal of Cleaner Production*, 309, Article 127427.
- Šulc R., Dítl P., 2021b, The Potential of Energy Savings in Oxygen Production by Pressure Swing Adsorption, *Chemical Engineering Transactions*, 86, 313-318.