CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš
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ISBN 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870054

Assessment of Hybrid Processes for Bio-Butanol Purification Applying Process Simulation

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Bio-butanol production based on ABE (acetone-butanol-ethanol) fermentation is facing increasing interest as a transport fuel, since it offers significant advantages to other bio-fuels. However, to ensure an economic operation two bottlenecks has to be overcome: (1) high cost of the fermentation substrate, and (2) high energy demand for butanol purification via distillation due to low solvent concentration in fermentation broth. While first bottleneck might be overcome by the use of alternative feedstock like lignocelluloses or agro-food-wastes, the latter can be targeted by introducing hybrid purification concepts, combining in-situ removal techniques with distillation. Experimental and literature data based on lab-scale size experiments operated with synthetical fermentation broth are used to parameterize an Aspen Plus® simulation to predict the energy demand for bio-butanol purification for three in-situ removal techniques coupled with distillation and to compare to a standalone distillation sequence: gas stripping, pervaporation and adsorption/desorption. Depending on the initial solvent content of fermentation broth, with 23.2 - 31.2 MJ/kg butanol the heat demand of the standalone distillation sequence is slightly below the energy content of butanol of about 36 MJ/kg. Applying gas-stripping and pervaporation before purification via distillation reduces the heat demand by 50 % to 13.6 - 16.8 MJ/kg and 12.0 - 14.5 MJ/kg butanol, respectively. Best result is shown by combining adsorption and distillation with an energy demand of 5.0 – 5.7 MJ/kg butanol. However, the advantageous low overall energy demand results from low efforts in the distillation step, only considering separation of butanol and water, but neglecting purification of acetone and ethanol obtained in ABE fermentation.

1. Introduction

Sustainable fuels and energy production based on renewable sources is one of the most important goals for today's society. Bio-butanol production based on ABE (acetone-butanol-ethanol) fermentation is facing increasing interest as a transport fuel, since it offers significant advantages to other bio-fuels. High specific energy, low corrosivity and good blending properties with conventional fuels make it a promising alternative for fossil-based gasoline and diesel (van der Merwe et al., 2013).

ABE fermentation has been done since the beginning of the 20th century, loosing economical competitivity with rising petrochemical industry (Maiti et al., 2015). In the last 30 years, with instable oil prices and rising interest in renewable energy, interest in bio-butanol production also returned. Two big bottlenecks remained towards an economic operation of the process: (1) high cost of the fermentation substrate (Kumar et al., 2012), and (2) high energy requirement for direct butanol distillation in the downstream due to low solvent concentration in fermentation broth caused by self-inhibition resulting in less than 15 g/l butanol produced during batch processes (Mariano et al., 2012).

While high substrate costs might be overcome by using lignocellulosic substrates and AFWs (agro-food wastes), hybrid separation concepts – combining in-situ removal techniques with distillation - are suggested to decrease energy demand. Implementation of in-situ removal of bio-butanol allows higher bacteria productivity by avoiding product inhibition, and by introducing additional separation steps to achieve higher feed concentration to distillation (Gottumukkala et al., 2017). Several in-situ removal techniques are in the centre of interest: adsorption, pervaporation, liquid-liquid extraction and gas stripping (Friedl, 2016).

While numerous experimental data are available assessing the performance of in-situ removal techniques, data for the whole hybrid purification sequence are scarce. Lack of data explains the wide ranging and inconsistent

Please cite this article as: Wukovits W., Kirchbacher F., Miltner M., Friedl A., 2018, Assessment of hybrid processes for bio-butanol purification applying process simulation , Chemical Engineering Transactions, 70, 319-324 DOI:10.3303/CET1870054

information on energy demand for ABE purification in literature (Outram et al., 2016). To provide consistent data for the energy demand, process simulation of hybrid purification processes, combining in-situ removal techniques coupled with distillation, are performed in Aspen Plus® v10 (AspenTech Inc., 2017).

Main objective of this work is to assess the heat demand of in-situ solvent removal techniques combined with distillation in a consistent way, based simulation models applying first separation principles and process specific parameters from experimental investigations, considering the complete hybrid purification chain. Sensitivity analysis concerning initial solvent concentration in fermentation broth together with reporting the contribution of the different separation steps to the overall heat demand of butanol purification will provide valuable information for selection of suitable hybrid processes as well as show opportunities for further reduction of heat demand.

2. In-situ removal processes and simulation models

Comparison of alternative processes for the removal and purification of butanol after ABE fermentation is difficult due to different process parameters and assumptions in upstream and downstream processing. Process simulation gives the opportunity to overcome the shortcomings of assessment of hybrid ABE purification processes (Outram et al., 2016):

- Inconsistent data due to differing process conditions and methods in experimental investigations
- Presentation of experimental data for in-situ removal technology, not considering the complete hybrid purification chain
- Focusing on separation of butanol/water system, not considering recovery and purification of acetone and ethanol
- Overcoming simplifications in estimating energy demand (e.g. only considering thermal energy of evaporation in pervaporation, neglecting power of vacuum pump)

Outram et al. (2016) presented a comparison of in-situ removal techniques for ABE fermentation based on simulation of the whole process chain of ABE fermentation. Energy demand is reported for upstream and downstream process steps resulting in an economic assessment. However, no further differentiation is done for the contribution of various purification steps to the overall downstream energy demand. Furthermore, set-up of models of in-situ removal techniques is based on simple component splitters (e.g. pervaporation), not considering the separation principle. Actual work overcomes this limitation using a membrane model based on experimental permeances obtained from membrane flux data instead of split factors, allowing rigorous modelling of the separation step. Furthermore, solvent removal via adsorption is based on experimental adsorption isotherms.

Three in-situ removal techniques considered for coupling with distillation for the purification of bio-butanol from fermentation broth are: gas stripping, pervaporation and adsorption/desorption.

2.1 Gas stripping

The most common technique for removal of butanol from ABE fermentation broth is gas stripping (Kumar and Gayen, 2011). An inert gas stream is injected in the reactor and volatile substances like acetone, butanol and ethanol are selectively removed from the broth without removing nutrients or harming cells (Dürre, 1998). The stripping gas carrying volatile substances leaves the reactor and is subjected to a separation process (e.g. condensation) to recover the acetone, butanol and ethanol. Stripping gas usually is N_2 or fermentation gas (CO_2 + H_2) (Yang and Lu, 2013), and can be recirculated reducing economic costs of the process. Stripping in an external column, instead of introducing the stripping gas into the reactor, might further improve the performance of the process by increasing the mass transfer.

The model of the stripping process consists of a column, allowing single stage or counter-current multistage stripping, a flash for condensation of stripped solvents as well as a fan and a heater/cooler to recycle the stripping-gas stream. Stripping is performed at 35°C, approximately representing fermentation temperature. Solvents are condensed at 4°C. Stripping gas flow is adjusted at 110 kg/kg butanol.

2.2 Pervaporation

Pervaporation is a thermally driven separation process applying dense membranes mostly of polymeric type. Transport through the membrane is driven by a difference in chemical potential between both sides of the membrane (feed/retentate side and permeate side; Kujawska et al., 2015) Current application requires pervaporation at only slightly elevated feed temperature (35°C fermentation temperature) due to economic disadvantage of significantly heating/cooling of the fermentation broth. Thus, the application of vacuum on the permeate side is required in order to enhance pervaporation performance.

Polydimethlysiloxane (PDMS) membranes are applied in pervaporation of solvents due to their good process performance (high selectivity), high hydrophobicity, and good thermal, chemical and mechanical stability

(Abdehagh et al., 2014). As alternative, polyoctylmethylsiloxane membranes (POMS) are in focus suggesting high potential for ABE upgrading (Rom et al., 2013).

The model of the pervaporation step is kept simple, consisting of an in-house, cross-flow, multicomponent membrane model (Rom et al., 2016), a vacuum pump and a condenser (flash unit). Pervaporation is performed at 35 °C and 10 mbar pressure. Condensation takes place at 4 °C. POMS membranes are considered in simulation based on experimental permeances due to a better separation performance compared to PDMS membranes (Kirchbacher et al., 2017).

2.3 Adsorption

Adsorption-based processes have been suggested to be among the most energy efficient options for n-butanol removal. Adsorbents are generally more biocompatible than solvents as well as fully immiscible and unsusceptible to emulsification. These features facilitate the adsorbent separation from cultures (Raganati et al., 2018). Selectivity of the adsorbent significantly impacts the performance of the recovery process because the ABE fermentation broth contains numerous species such as substrates and nutrients (Dürre, 2007). Additional downstream processing is required to ultimately recover the adsorbed bio-butanol:

- Drying step to remove sticking fermentation broth before desorption step
- Desorption step to remove butanol from adsorbent

Regeneration of the adsorbent by using thermal swing operation is probably the most used regeneration technique (Oudshoorn et al., 2012). Thermal swing operation uses the shift in adsorption behaviour as a function of temperature. Although the operating steps in terms of desorption and regeneration play an important role in a complete butanol separation process, most reports focus on butanol adsorption on specific adsorbents (Lin et al., 2012). Only a few articles have considered butanol desorption behaviour and resin regeneration (Qureshi et al., 2005).

Modelling of the adsorption step includes a user defined adsorption unit, drying step, desorption step and a condenser to liquefy the removed/desorbed solvents. This modelling approach follows Outram et al. (2016) representing the adsorbent as solid stream. However, instead of representing adsorption as a series of conversion reactors, a user defined unit allows single stage or multistage adsorption based on adsorption isotherms.

Amberlite XAD-7 was selected as adsorbents showing high butanol binding capacity both with single component and multicomponent adsorption. For the adsorption step equilibrium is assumed, represented by adsorption isotherms taken from Raganati et al. (2018). Adsorption takes place at fermentation temperature (35°C). In the drying step remaining fermentation broth (0.5 mL/g adsorbents) is removed at 60°C. Furthermore, as experimental results show, acetone and ethanol are desorbed. In the following desorption step remaining butanol and water is removed from the adsorbent and liquefied in a subsequent condenser (flash unit) at 4°C.

3. Results and discussion

Process simulation is used to assess the energy demand of 3 different hybrid ABE purification options, based on experimental results, literature data and general engineering assumptions. A maximum driving force is assumed for all in-situ removal options, operating processes at high solvent concentration with a removal rate near the production rate of solvent. Results represent a minimum energy demand as benchmark for sensitivity and further process analysis. Generated results include heat and power demand (e.g. fan, vacuum pump) of the main removal steps. Cooling demand for condensation is neglected to allow comparison to literature data. No process integration is considered provide an easier comparison between different purification steps.

Table 1: Parameters of distillation sequence for ABE purification

Column	Stages	Feed stage	Specification
Broth column	45	1	97.5 % ABE recovery
Acetone column	30	15	99.5 % acetone recovery, 99.5 w% acetone in product stream
Ethanol column	40	10	98 % ethanol recovery, 60 w% ethanol in product stream
Butanol columns (2)	10	1	99.5 % butanol recovery, 99.5 w% butanol in product stream

Models of gas stripping, pervaporation and adsorption described in section 2 are combined with distillation for further purification of butanol, acetone and ethanol. The distillation sequence for ABE upgrading consisting of 5 columns is simulated according to literature (Outram et al., 2016). Column data and specifications for separation are summarized in Table 1. The same column set up is used for simulation of the stand-alone distillation process as well as the hybrid processes with gas stripping and pervaporation. For the hybrid process with adsorption the distillation sequence is reduced to 2 butanol columns. During simulation the number of stages was kept constant whereas the reflux ratio of columns was adjusted to meet the specifications defined in Table 1. Product purities for acetone and butanol are selected similar to settings in literature (van der Merwe et al. (2013): 98.0 and 99.5 w%, respectively; Outram et al. (2016): 99.5 w% for both components). However, product concentration for ethanol at 60 w% is set considerably lower (van der Merwe et al. (2013): 99 w% - although not to be reachable with all separation sequences proposed in the paper; Outram et al. (2016): > 80 w%). Due to the low content in the fermentation broth (10 % to the overall solvent content) and the known high energy demand for purification, a concentration level suitable for further processing in existing ethanol facilities or use within the overall ABE fermentation process for feedstock pre-treatment (Weinwurm et al., 2015) is selected.

Figure 1 compares the energy demand of investigated hybrid processes for varying butanol content in the feed stream of 1.0 - 1.5 (maximum due to self-inhibition) w% butanol. Solvent ratio in the feed stream is kept constant at A: B: E = 3: 6: 1.

Heat demand of the standalone distillation sequence is slightly below the energy content of butanol of 36 MJ/kg. Applying gas-stripping and pervaporation before final purification via distillation reduces the heat demand by 50 %. Energy demand of the hybrid process with stripping is only slightly higher than that with pervaporation. However, comparing both separation options it has to be considered that solvent recovery in gas stripping with 60-70 % is considerably lower than in pervaporation with almost 100 %. Best results are shown by combining adsorption and distillation with an energy demand of only a fifth of standalone distillation and a butanol recovery of almost 100 %.

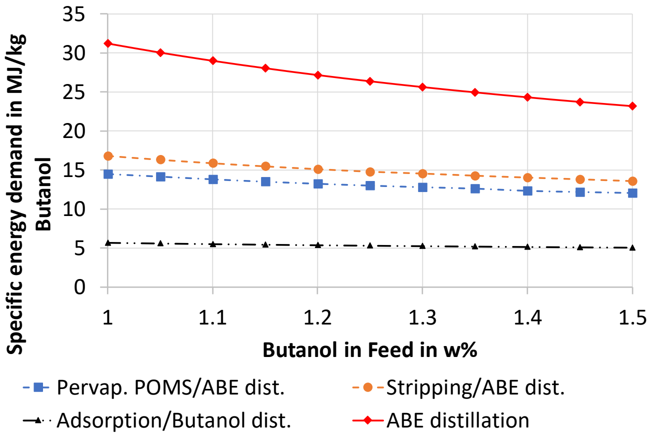

Figure 1: Comparison of energy demand of simulated hybrid butanol purification processes with standalone distillation sequence

In Figures 2 and 3, details of the contribution of involved separation steps to the overall energy demand of ABE purification are given. The advantageous low overall energy demand of adsorption results from low efforts in the distillation step only considering separation of butanol and water, but neglecting purification of acetone and ethanol obtained in ABE fermentation. Energy demand of pervaporation and adsorption step is comparable at 1.0 g/L butanol content of the fermentation broth. However, energy demand of adsorption is remaining almost constant (4.3 – 3.8 MJ/kg butanol) while energy demand of pervaporation decreases (4.7 – 2.4 MJ/kg butanol) with increasing butanol concentration. The energy demand of gas stripping step is highest, due to the power demand for pressurizing the high gas flow rate necessary for the stripping process.

Differences in heat demand in the columns of the distillation sequence are connected with the selectivity and/or recovery of in-situ solvent removal step. A higher heat demand is needed in the broth column after gas stripping since more water is removed compared to pervaporation and adsorption. Heat demand for ethanol and especially acetone separation/purification is lower due to higher losses for these solvents compared to butanol caused by their higher vapour pressure. Contribution of heat demand of the butanol column is comparable for solvent removal via gas-stripping, pervaporation and adsorption.

Although ethanol represents only 10 % of solvent content in fermentation broth, removal from butanol stream and purification to a content of 60 w% needs a higher specific heat demand than separation of acetone and the final purification step of butanol (Figures 2a and b). Whereas the heat demand to upgrade ethanol up to 80 w%

only slightly increases, an increase by 10 % of overall heat input has to be considered when upgrading to an ethanol content of 90 w%.

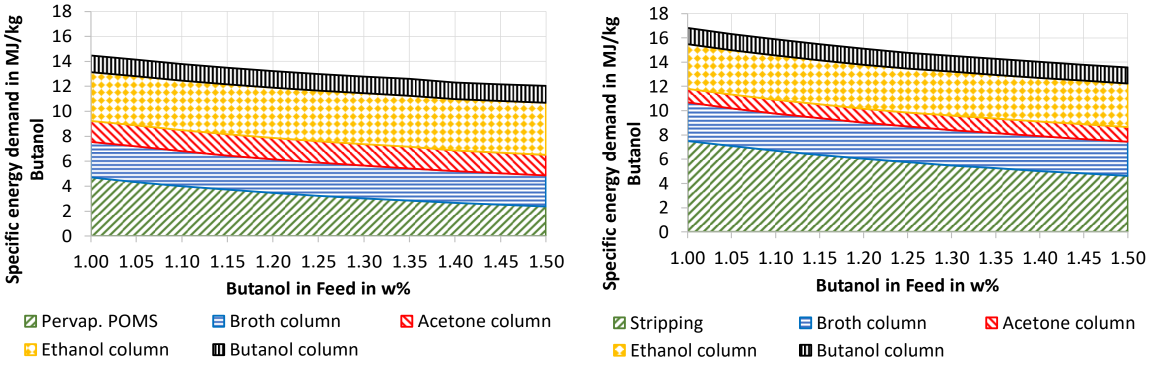

Figure 2: (a) Details energy demand hybrid process pervaporation/distillation. (b) Details energy demand hybrid process gas stripping/distillation

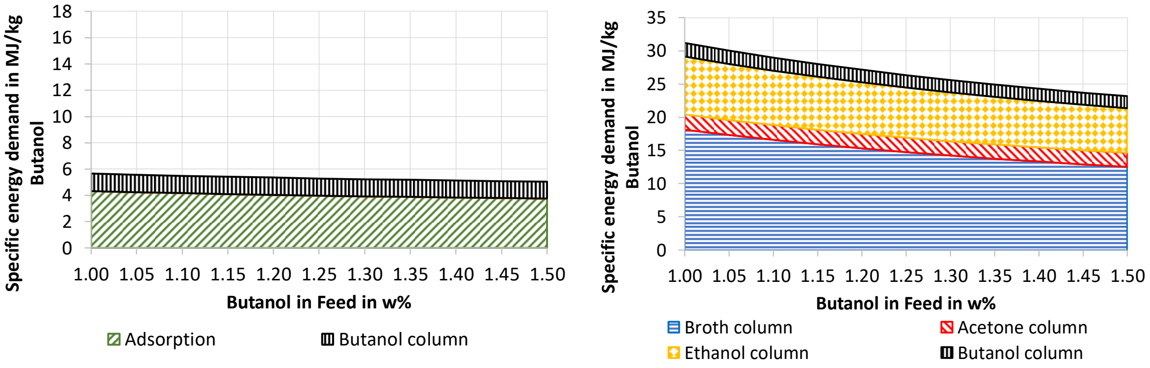

Figure 3: (a) Details energy demand hybrid process adsorption/distillation. (b) Details energy demand standalone distillation

4. Conclusions

Assessment of hybrid processes for bio-butanol purification via process simulation shows a considerable reduction of energy demand compared to a standalone distillation sequence. Combining distillation with preceding gas stripping and pervaporation reduces the energy demand by a half, whereas preceding adsorption reduces energy demand by 80 %. Process simulation promises an objective comparison of results of investigated separation options, considering the complete hybrid purification chain.

Comparison of the different contributions of separation steps to the overall heat demand of butanol purification provides valuable information for selection of suitable hybrid processes as well as show opportunities for further reduction of heat demand. Low energy demand in the hybrid process combining distillation and adsorption is mainly caused by the fact that in the distillation step only separation of butanol and water is considered, but acetone and ethanol are not recovered and processed. Furthermore, the large contribution of ethanol separation to the overall head demand is visible, suggesting a separation sequence de-coupling ethanol and acetone purity from the main separation path.

More reliable results are expected from experimental results coupling in-situ removal techniques with the fermentation step. However, detailed prediction of heat and energy demand based on lab-experiments remains difficult. Furthermore, effects of applied hybrid upgrading technologies on the upstream process should be considered including options for heat integration.

Acknowledgments

Results are elaborated within project Waste2Fuels receiving funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 654623. We knowledge the use of experimental data for parametrizing our simulation models from Waste2Fuels partners Instituto Technologico Agrario (Leon, Spain), Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Università degli Studi di Napoli Federico II (Napoli, Italy) and Instituto di Ricerche sulla Combustione– Consiglio Nazionale delle Ricerche (Napoli, Italy)

References

Abdehagh N., Tezel F.H., Thibault J., 2014, Separation techniques in butanol production: Challenges and developments, Biomass and Bioenergy, 60, 222–246.

Dürre P., 1998, New insights and novel developments in clostridial acetone/butanol/isopropanol fermentation, Applied Microbiology and Biotechnology, 49, 639–648.

Dürre P., 2007, Biobutanol: an attractive biofuel. Biotechnology Journal, 2, 1525–1534.

Friedl A., 2016, Downstream process options for the ABE fermentation. FEMS Microbiology Letters, 363, 1–5.

Gottumukkala L.D., Haigh K., Görgens J., 2017, Trends and advances in conversion of lignocellulosic biomass to biobutanol: Microbes, bioprocesses and industrial vitality, Renewable & Sustainable Energy Reviews, 76, 963-973.

Kirchbacher F., Miltner M., Friedl A., Wukovits W., 2017, Impact of membrane material properties on the performance of a combined pervaporation and distillation process for biobutanol concentration, 10th World Congress of Chemical Engineering –WCCE10, Barcelona, Spain, 01.-05. October 2017.

Kujawska A., Kujawski J., Bryjak M., Kujawski W., 2015, ABE fermentation products recovery methods - A review, Renewable & Sustainable Energy Reviews, 48, 648–661.

Kumar M. and Gayen K., 2011, Developments in biobutanol production: New insights, Applied Energy, 88, 1999–2012.

Kumar M., Goyal Y., Sarkar A., Gayen K., 2012, Comparative economic assessment of ABE fermentation based on cellulosic and non-cellulosic feedstocks, Applied Energy, 93, 193–204.

Lin X., Wu J., Fan J., Qian W., Zhou X., Qian C., Jin X., Wang L., Bai J., Ying H., 2012, Adsorption of butanol from aqueous solution onto a new type of macroporous adsorption resin: Studies of adsorption isotherms and kinetics simulation, Journal of Chemical Technology and Biotechnology, 87, 924–931.

Maiti S., Sarma S.J., Brar S.K., Bihan Y.L., Drogui P., Buelna G., Verma M., Soccol C.R., 2015, Novel spectrophotometric method for detection and estimation of butanol in acetone–butanol–ethanol fermenter, Talanta, 141, 116–121.

Mariano A.P., Dias M.O.S., Junqueira T.L., Cunha M.P., Bonomi A., Filho R.M., 2012, Butanol production in a first-generation Brazilian sugarcane biorefinery: Technical aspects and economics of greenfield projects, Bioresource Technology, 135, 316–323.

Oudshoorn A., van der Wielen L.A.M., Straathof A.J.J., 2012, Desorption of butanol from zeolite material. Biochemical Engineering Journal, 67, 167–172.

Outram V., Lalander C.-A., Lee J.G.M., Davis E.T., Harvey A.P., 2016, A comparison of the energy use of in situ product recovery techniques for the Acetone Butanol Ethanol fermentation, Bioresource Technology, 220, 590–600.

Qureshi N., Hughes S., Maddox I.S., Cotta M.A, 2005, Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption, Bioprocess and Biosystems Engineering, 27, 215–222.

Raganati F., Procentese A., Olivieri G., Russo M.E., Salatino P., Marzocchella A., 2018, Bio-butanol separation by adsorption on various materials: Assessment of isotherms and effects of other ABE-fermentation compounds, Separation Science and Technology, 191, 328-339.

Rom A., Esteve D., Friedl A., 2013, Organophilic pervaporation of butanol from an aqueous solution with POMS, Chemical Engineering Transactions, 35, 1315–1320.

Rom A., Miltner A., Wukovits W., Friedl A., 2016, Energy saving potential of hybrid membrane and distillation process in butanol purification: Experiments, modelling and simulation, Chemical Engineering and Processing - Process Intensification, 104, 201–211.

Van der Merwe A.B., Cheng H., Görgens J.F., Knoetze J.H., 2013, Comparison of energy efficiency and economics of process designs for biobutanol production from sugar cane molasses, Fuel, 105, 451-458.

Weinwurm F., Drljo A., Friedl A., 2015, Lignin concentration by nanofiltration and precipitation in a lignocellulose biorefinery, Chemical Engineering Transactions, 45, 901-906.

Yang S.-T. and Lu C., 2013, Extraction-fermentation hybrid (Extractive fermentation), Chapter in: Ramaswamy S., Huang H.J., Ramarao B.V. (Eds.), Separation and purification technologies in biorefineries. John Wiley & Sons, Chichester, UK, 409-437.