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High permeance composite hollow fiber membranes for CO_2 capture from flue gas

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Abstract: Compared to the conventional technologies such as amine absorption for CO_2 capture from industrial sources such as flue gas, membrane separation process has unique advantages of being environmentally benign, lower maintenance and smaller footprint. Composite membranes with high CO_2 permeation rate have great potential to capture CO_2 from flue gas economically competitive.

This paper reports our development in composite hollow fiber membranes with ultra-thin selective layer by using ultrafiltration hollow fibres as substrate, coated with multiple layers of gutter, selective and protective layers, using commercially available (polyether (PE)-block- polyamide (PA) copolymer) Pebax® as base material for the selective layer. The optimized fabrication condition was evaluated based on screening of substrates, selection of gutter layer material as well as evaluation of the selective material and dip-coating conditions against the gas separation performance with CO_2 permeance and CO_2/N_2 selectivity. Consistently high CO_2 permeance up to 560 GPU and CO_2/N_2 selectivity as high as 45 were achieved with composite membranes fabricated with pure Pebax® as selective layer while improvements were further achieved with addition of nanoparticles into the selective solution for dip-coating.

Keywords: CO₂ capture, composite membrane, hollow fiber, flue gas.

1 Introduction

The membrane technology can be economically competitive with other CO_2 capture technology when high separation performance can be achieved and maintained in industrial environment. One issue related to gas separation membranes is the trade-off between permeability and selectivity, in that membranes that possess high permeance normally suffer lower selectivity and vice versa. Thin film composite (TFC) membrane with the advantages of utilising microporous membrane as substrate with low transport resistance and highly selective thin layer of material as separation layer could significantly improve the productivity while maintain good selectivity.

Polymeric material containing groups with high affinity to CO_2 molecules, such as those with polyethylene oxide (PEO) containing block copolymers, with semi-crystalline hard phase for robust mechanical strength and good chemical and thermal resistance and PEO containing soft phase with strong CO_2 affinity for excellent CO_2/N_2 selectivity have been identified as good candidate for CO_2 separation membranes. In particular, a commercially available poly(ethylene oxide)-Poly(amide) polymers, commercial name Pebax® have shown great potential for this development. Our earlier results using Pebax®1657 and 1074 as dense membrane material have shown that highly selective membranes could be fabricated with both of those grades of polymers [1].

This study aimed to explore the gas separation performance of composite hollow fiber membranes using Pebax® based materials as thin film composite selective layer in order to identify issues related with translating the good separation performance observed in dense membrane to the thin film composite membranes. Apart from the properties of the Pebax® solution (concentration, additive doping and viscosity) used as selective layer coating, other parameters such as selection of substrate, materials for gutter layer coating can also affect the resulted membrane and were also evaluated in this study. Blending of Pebax® with inorganic particles with high gas permeability as additive to the selective material was also evaluated for their capacity to further improve CO_2 permeation rate.

2 Method

Fabrication of composite hollow fiber was conducted with a purpose-built dip coating facility for hollow fibres, controlled with a stepper motor programmed and controlled with a computer, with the flexibility to operate at different fiber immersion speed, control of the resident time of fibres in the coating solution and the control of fiber withdraw speed from the solution, as illustrated in Figure 1 (a).

The selection of hollow fiber substrate was based on their material that was compatible with the coating solutions, physical geometry that provides mechanical strength to withstand operating pressure of the gas feed, pore size that affects the penetration of the coating solution and resistance to gas transport.

Material for gutter layer coating was selected based on their capability to form thin film on the substrate surface without deep penetration into the substrate with minimum addition to the overall transport resistance. Materials with very high permeability to CO_2 such as polydimethylsiloxane (PDMS) and poly((trimethylsilyl) propyne) (PTMSP) were good candidates and were evaluated in this study. The chemical structures of PDMS, PTMSP were presented in Figure 2 together with that of Pebax®.

ZIF-8 formed with both metal and organic components (Figure 1(b)) was synthesized at rapid room temperature condition followed by washing and centrifugation before suspending in 70/30 wt./wt. ethanol/water solution used for PEBAX® polymer to be blended with the polymer solution by way of priming for fabrication of composite membrane using nano-particle blended selective layer.

Evaluation of the membrane characteristics were performed with scanning electron microscopy (SEM) for comparison of the composite layer thickness with different materials at different condition. The penetration of the gutter layer into the membrane pores was represented through the energy dispersive X-ray (EDX) spectroscopy analysis of Si elements profile in the region adjacent to the membrane pores in the top surface.

Gas separation performance of the selected membranes was evaluated with pure gases in the context of flue gas at the constant pressure gas permeation rig at pressure of 100 psi and temperature of 35 °C.

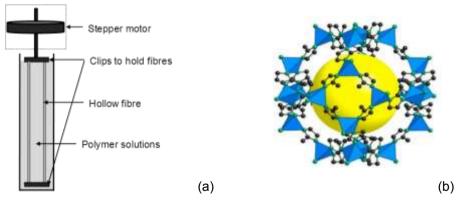


Figure 1(a) Schematic representation of the dip coating facility and (b) structure of ZIF-8. Zn metal is shown in blue polyhedra, while the organic linker is shown in black ball and stick. The yellow ball inside represents the cage of particle (Reproduced from [2] with permission).

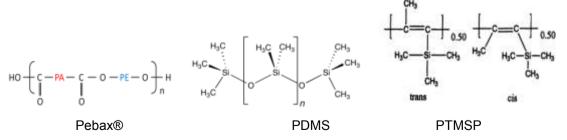


Figure 2 Chemical structures of Pebax®, (Pebax®1657 was made of PA6 while Pebax®1074 was made of PA12), PDMS and PTMSP.

3 Results and discussion

For the selected substrate made of PVDF microporous hollow fiber, (inferior results obtained with PES hollow fiber are not included in this paper), coating of the gutter layer with PTMSP resulted thinner overall thin film layer thickness compared with that obtained with PDMS as gutter as shown in Figure 3. The beneficial thin layer in PTMSP coated membrane was probably caused by less pore penetration of PTMSP solution during the coating process as indicated by the much smaller presence of element of Si (present in both PDMS and PTMSP) inside the membrane substrate as shown in Figure 4.

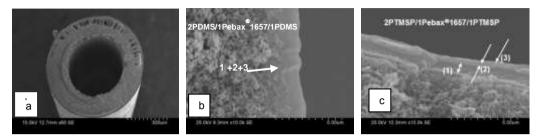


Figure 3 SEM images of the hollow fiber substrate (a), top layer of fiber coated with PDMS as substrate and gutter layer (b) and top layer of fiber coated with PTMSP as gutter (c).

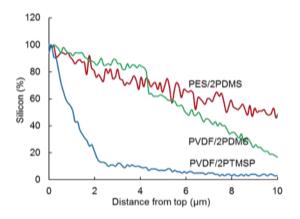


Figure 4: Relative silicon concentration profile within 10 µm depth obtained from EDX analysis for the PVDF and PES hollow fibers coated with PDMS and PTMSP as gutter layers.

Table 1 CO_2 permeance and CO_2/N_2 selectivity of composite hollow fiber membranes using PVDF hollow fiber as substrate and PDMS and PTMSP as gutter layer and comparison with dense membrane performances

Membrane (substrate +)	CO ₂ (GPU)	N ₂ (GPU)	CO ₂ /N ₂
4PDMS/1Pebax [®] 1657/1PDMS	76 (±7.2)	1.22 (±0.45)	66 (±15.6)
4PDMS/1Pebax [®] 1074/1PDMS	174 (±16.4)	3.74 (±0.50)	47 (±1.7)
4PTMSP/1Pebax [®] 1657/1PTMSP	101 (±6.6)	1.18 (±0.07)	86 (±4.33)
4PTMSP/1Pebax [®] 1074/1PTMSP	560 (±17)	12.07 (±0.35)	46 (±1.83)
4PTMSP/1Pebax [®] 1657+10%ZIF8/PTMSP	250	7.8	32.1
4PTMSP/2Pebax [®] 1074+10%ZIF8/Pebax [®] 1074	343	10.8	32
4PTMSP	3296 (±345)	598 (±75)	5.5 (±0.16)
Pebax [®] 1657 dense membrane	49 Barrer	0.60 Barrer	82
Pebax [®] 1074 dense membrane	70 Barrer	1.11 Barrer	63
PTMSP dense membrane	56145 Barrer	10122 Barrer	5.6

Gas separation performance obtained with pure gas tests conducted at room temperature given in Table 1 suggested that

- Higher CO₂ permeance was generally achieved with the composite membranes using Pebax®1074 as coating material compared with that of Pebax®1657, while higher selective was achieved with membranes using Pebax®1657 as selective material. This observation correlates with the relative performance of the dense membranes made with those materials.
- 2) Much higher CO₂ permeance was achieved in membranes using PTMSP as gutter material compared with that of PDMS, likely due to the penetration of PDMS into the substrate pores, results in increased resistance to gas transport.
- 3) Blending of nanoparticle ZIF-8 into Pebax[®]1657 as selective material has resulted in increased CO₂ permeance, while selectivity was slightly compromised. On the other hand, addition of ZIF-8 into Pebax®1074 has led to both lower CO₂ permeance and the selectivity compared to the membrane without the nano-particles, possible due to the adverse change of the micro-phase separated structure of the thin selective layer by the presence of ZIF-8.

Comparison of the performance of the multi-layer composite hollow fiber membranes fabricated in this study with various result found in the literature indicated that the results achieved with the PTMSP/Pebax®1074 in this study is the highest with the hollow fiber membranes, as shown in Figure 5. MTR PolarisTM is a well-known commercial thin film composite spiral wound membrane with high CO2 permeance achieving 1000 GPU and CO2/N2 selectivity of 50 (at 30 °C). The economic assessment conducted by Merkel et al. concluded that with this performance, CO2 capture cost could be reduced to around \$33 with the technical targets of 90 % carbon capture at 5 bar pressure ratio and membrane skid cost of \$50, making membrane technology competitive with the conventional amine scrubbing process at a cost of \$40-\$100 [3]. Given the lower cost of the hollow fiber membranes compared with the spiral wound module [4], the performance of composite membrane developed in this study could reach the competitive cost range. However, further study of those membranes in the context of real flue gas, particular their tolerance to the presence of water content is recommended.

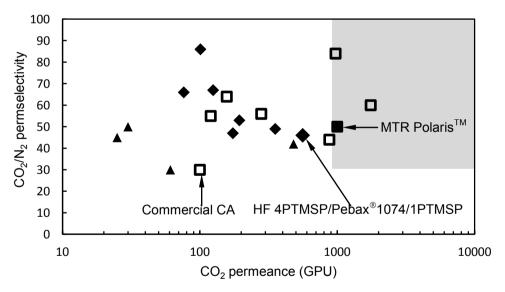


Figure 5 High performance thin film composite membranes reported in literatures. \Box flat sheet [3, 5-10] \blacktriangle hollow fibre [11-14]; \blacklozenge this study (at room temperature) the grey frame indicates the target region defined by MTR for high performance TFC membrane.

Conclusions and recommendations

Composition hollow fiber membranes developed in this study have shown very promising performance to CO_2 capture. Factors influence the separation performance of the composite membrane were evaluated and identified, which include materials for substrate, gutter layer and the selective materials, avoidance of pore penetration, and formation of thin layer of coating are crucial for high CO_2 permeance. Addition of nanoparticles could further improve CO_2 permeance with some selective materials and are currently under investigation for the optimised performance.

Micro-phase structure of the composite membrane will be further investigated to identify the possible difference between the micros structure of the dense membrane and that of the thin film composite membrane.

Acknowledgements

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Presenting author biography

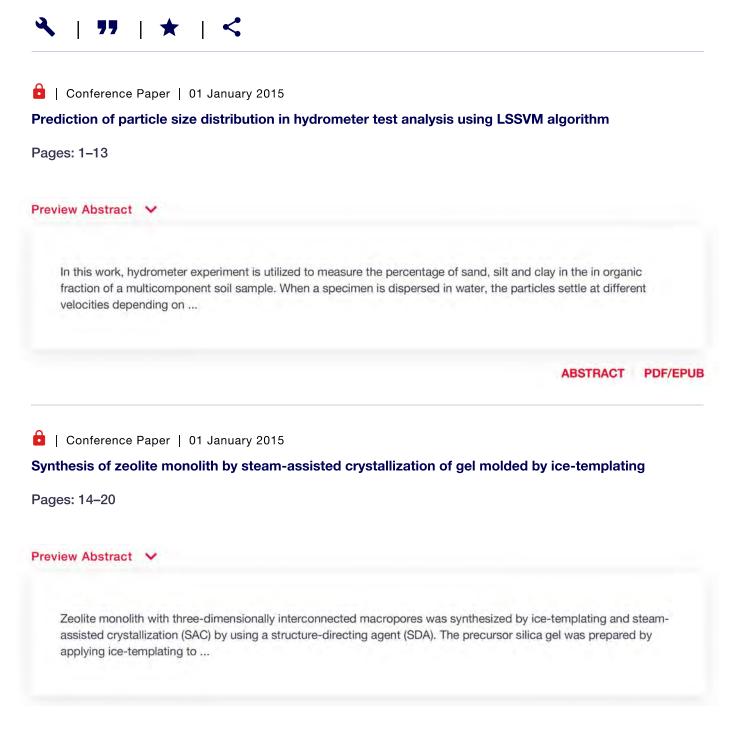
Dr Hongyu Li is a research fellow in UNESCO Centre for Membrane Science and Technology, School of Chemical Engineering, UNSW Australia. She has over 20 year's research experience in membrane science and technology in microfiltration, ultrafiltration and membranes for gas separation. Her expertise includes mechanisms of particle deposition and membrane fouling, fluid dynamics and their influence in membrane fouling and cleaning process. In the past 8 year, she has been conducting research in CO_2 capture using gas separation membranes in development of high performance hollow fiber membranes and composite membranes for CO_2 capture from natural gas and from flue gas.

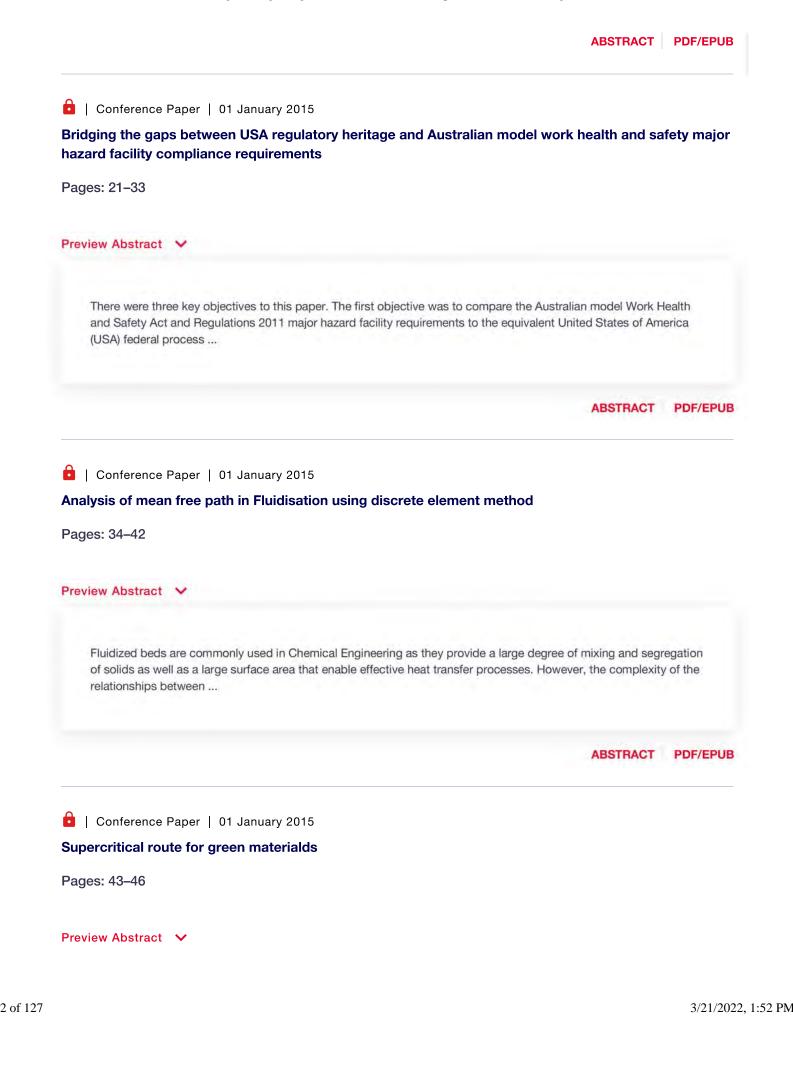


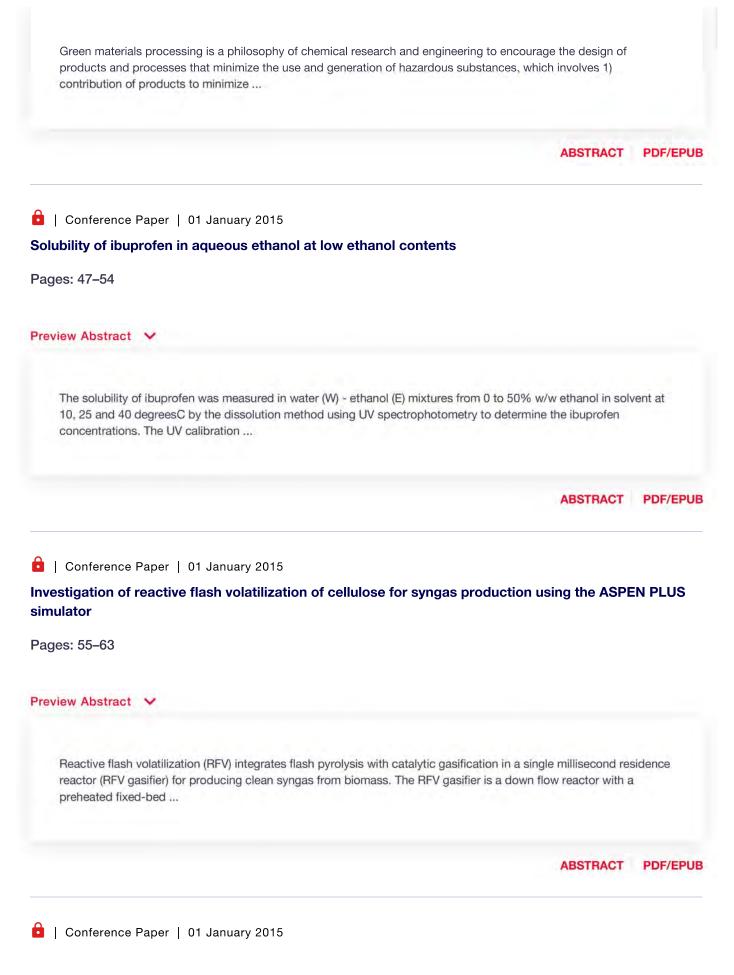
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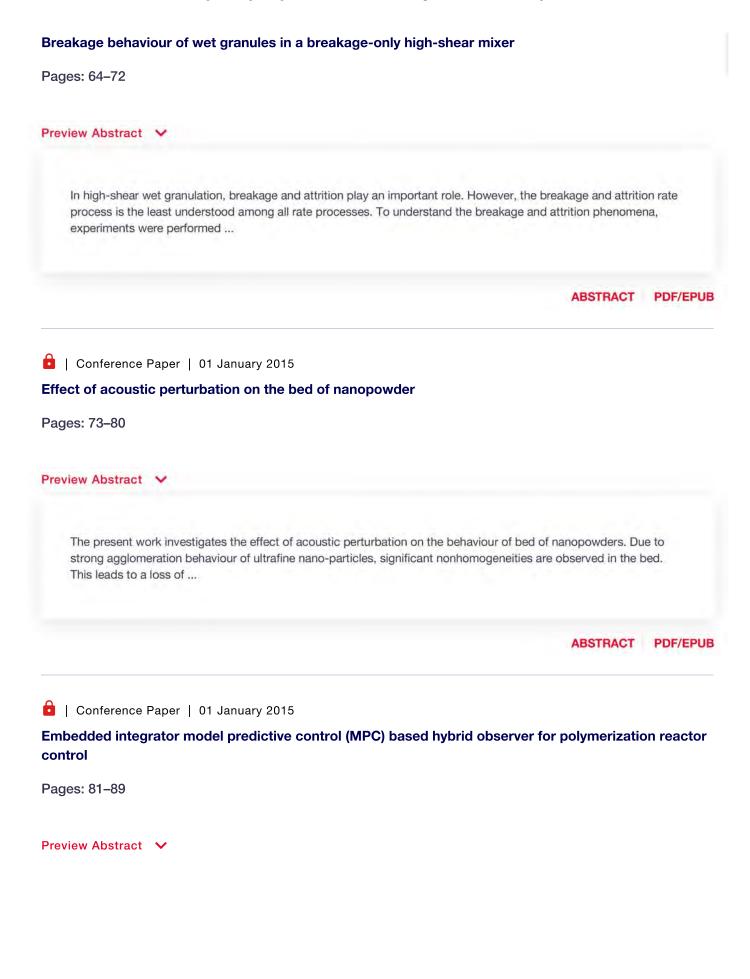
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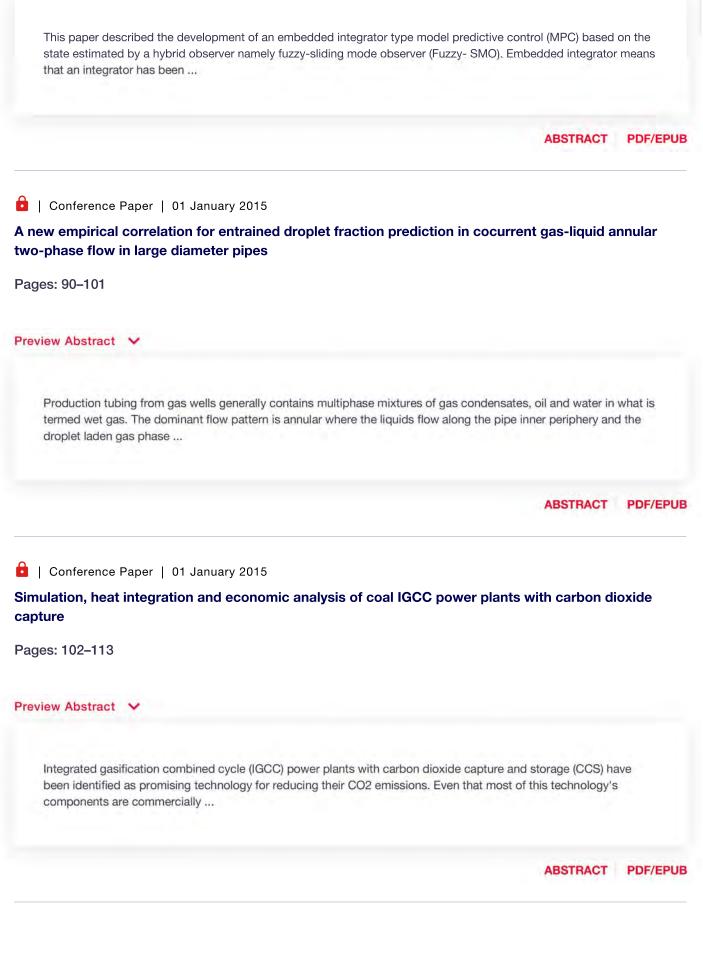






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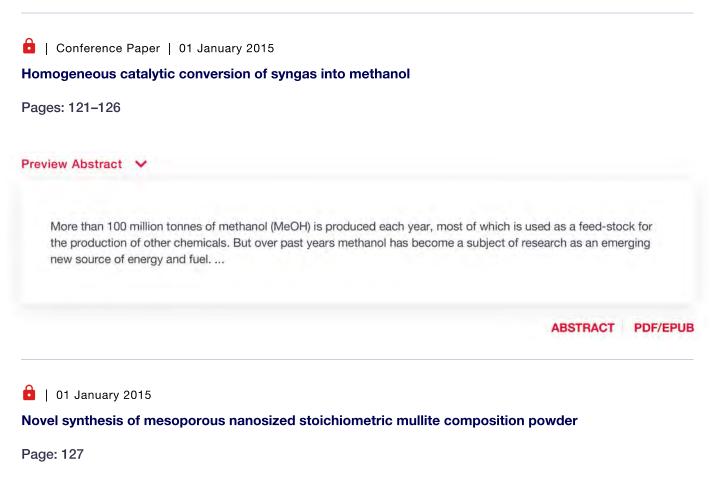
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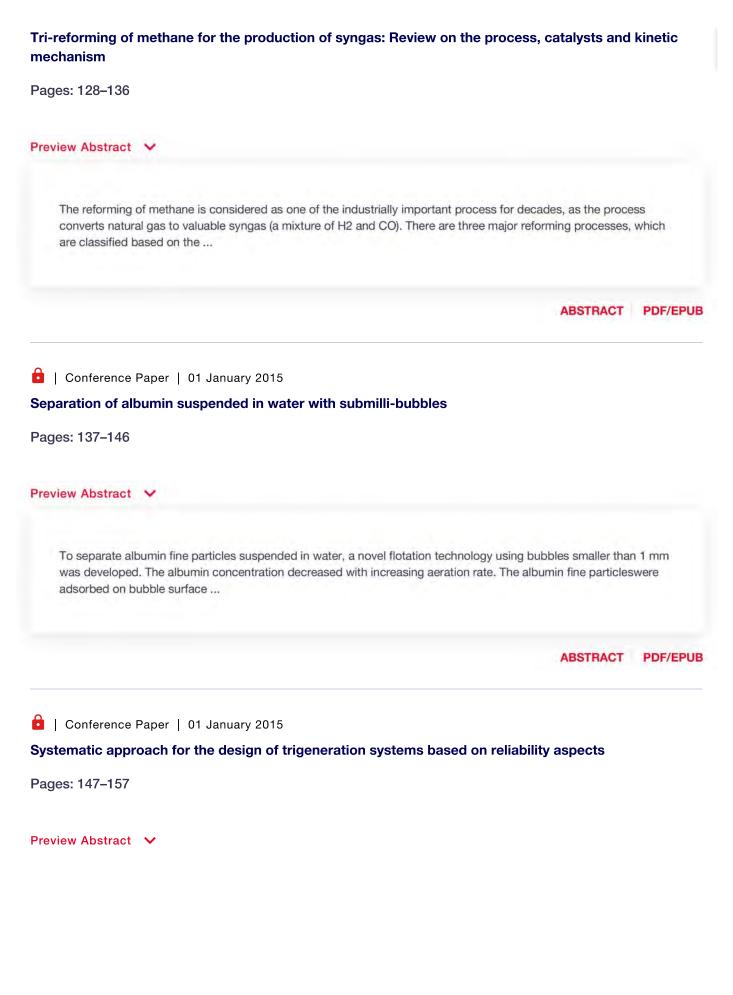
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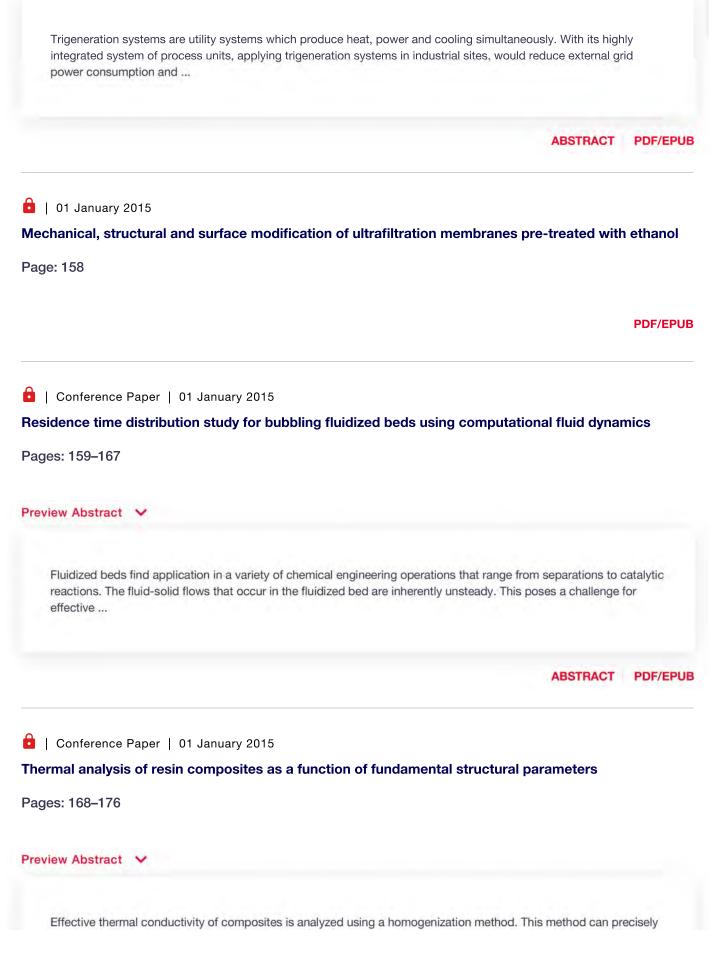
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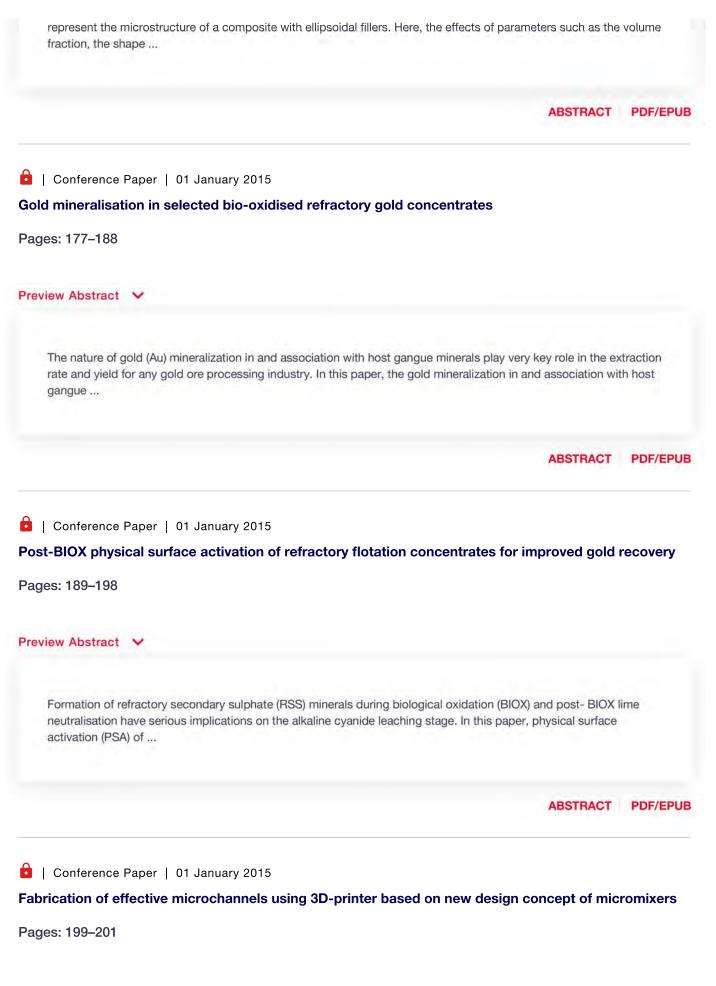


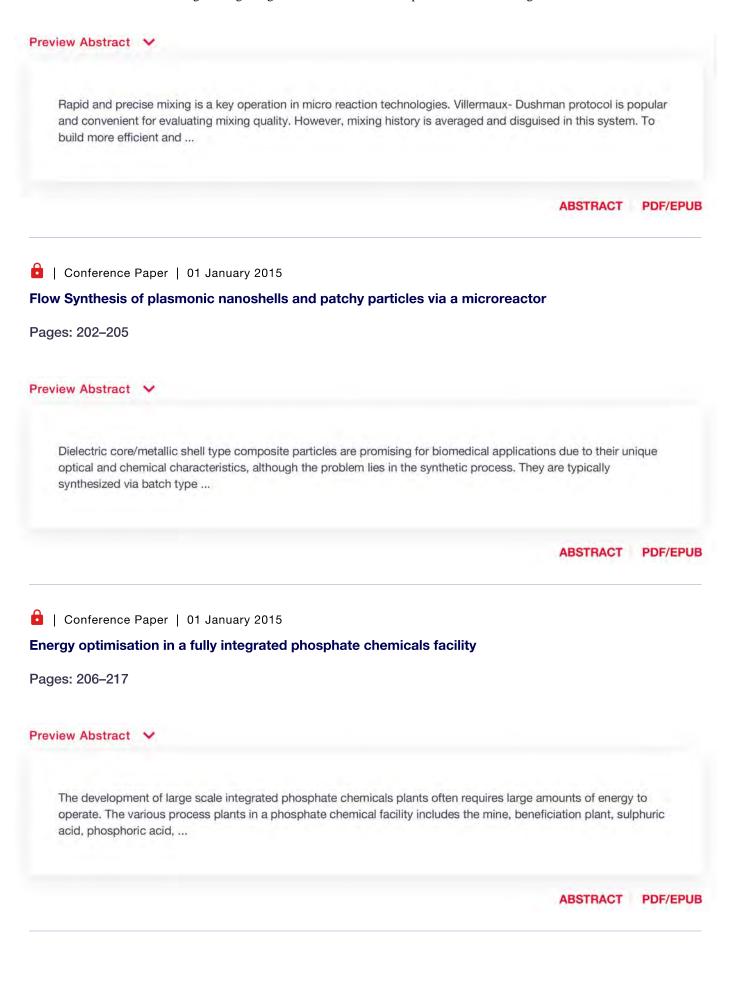
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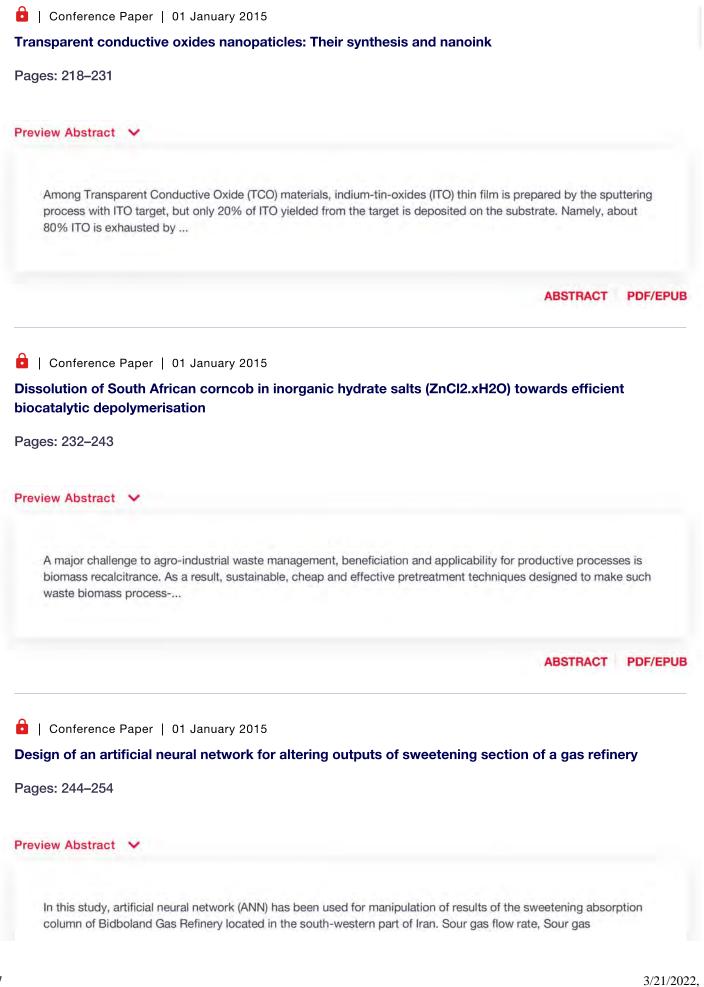
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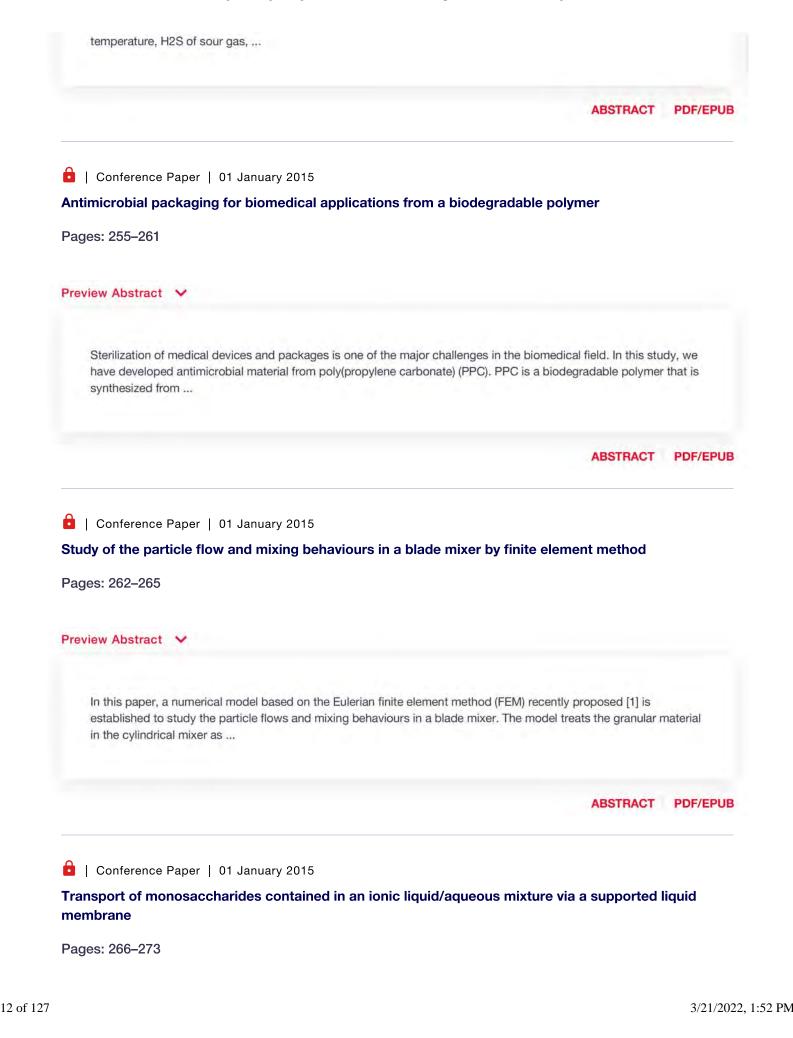


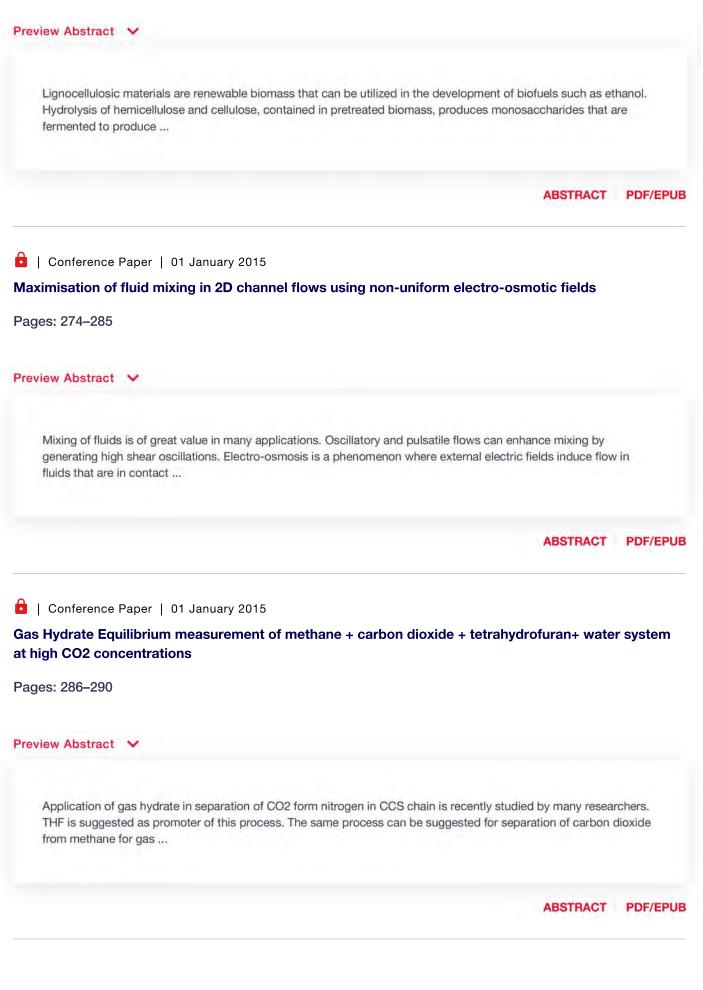


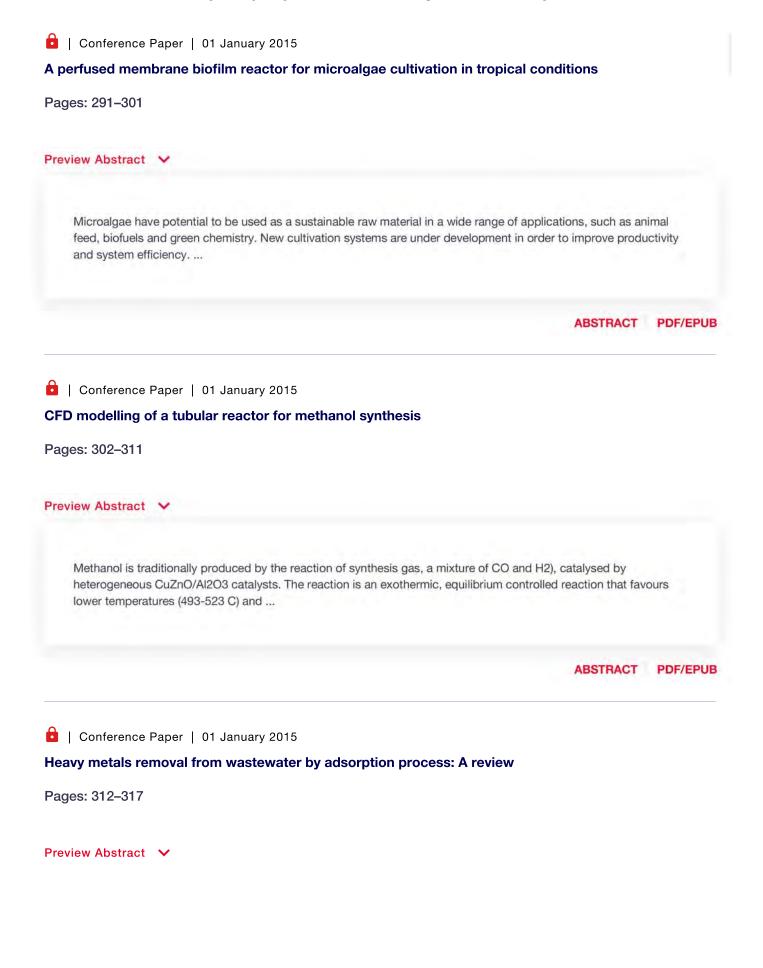


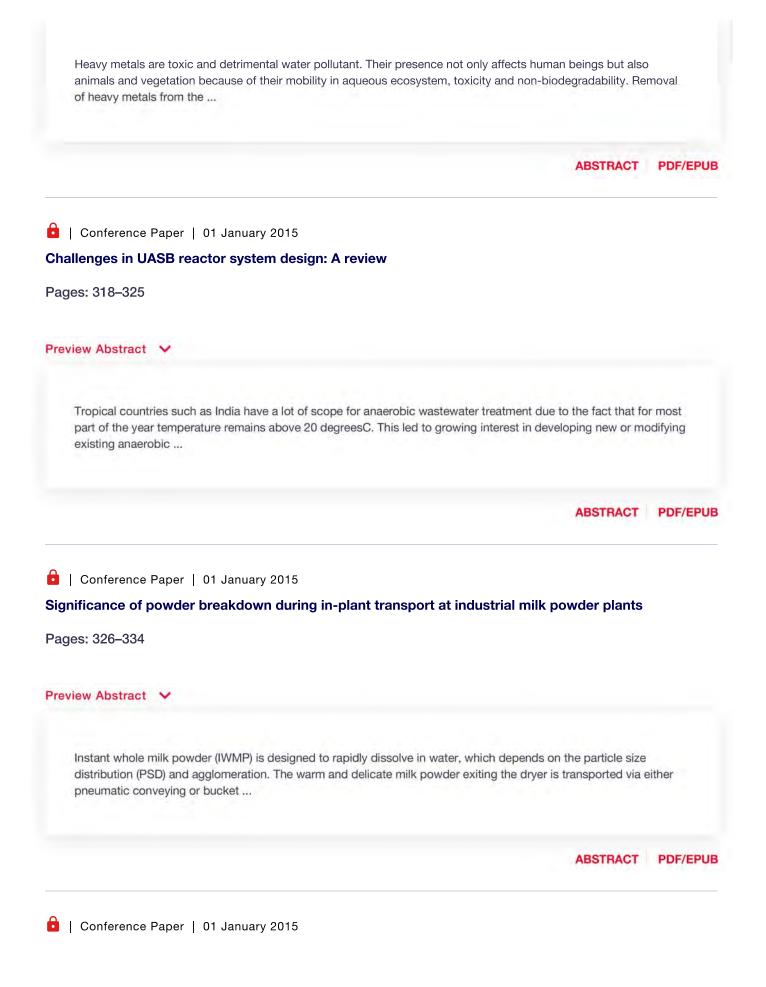


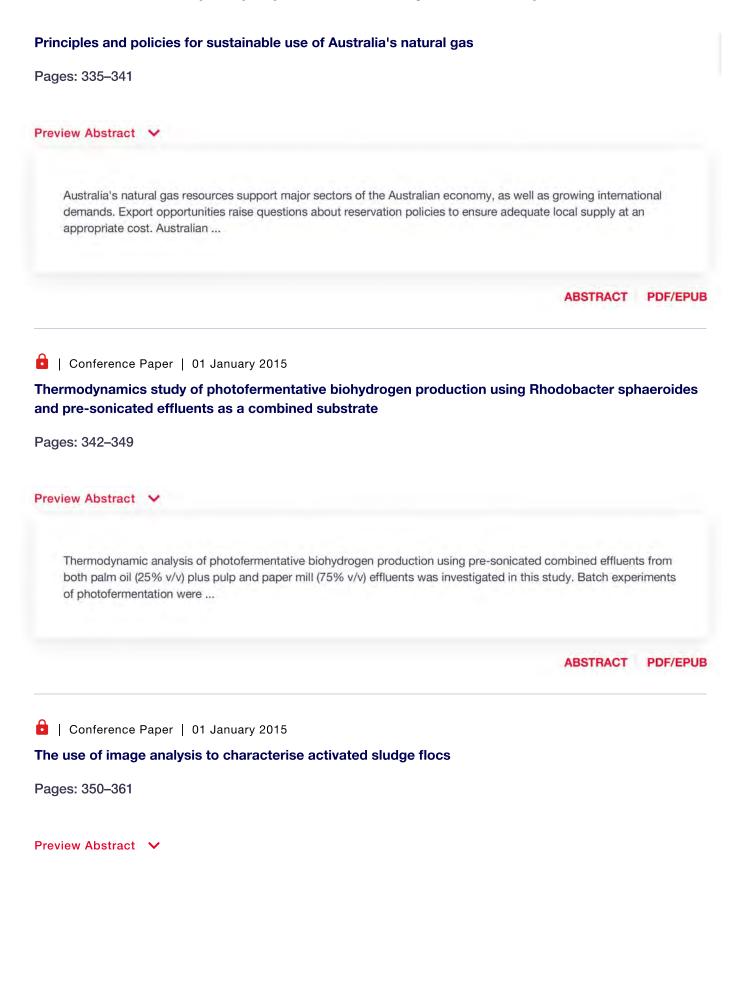


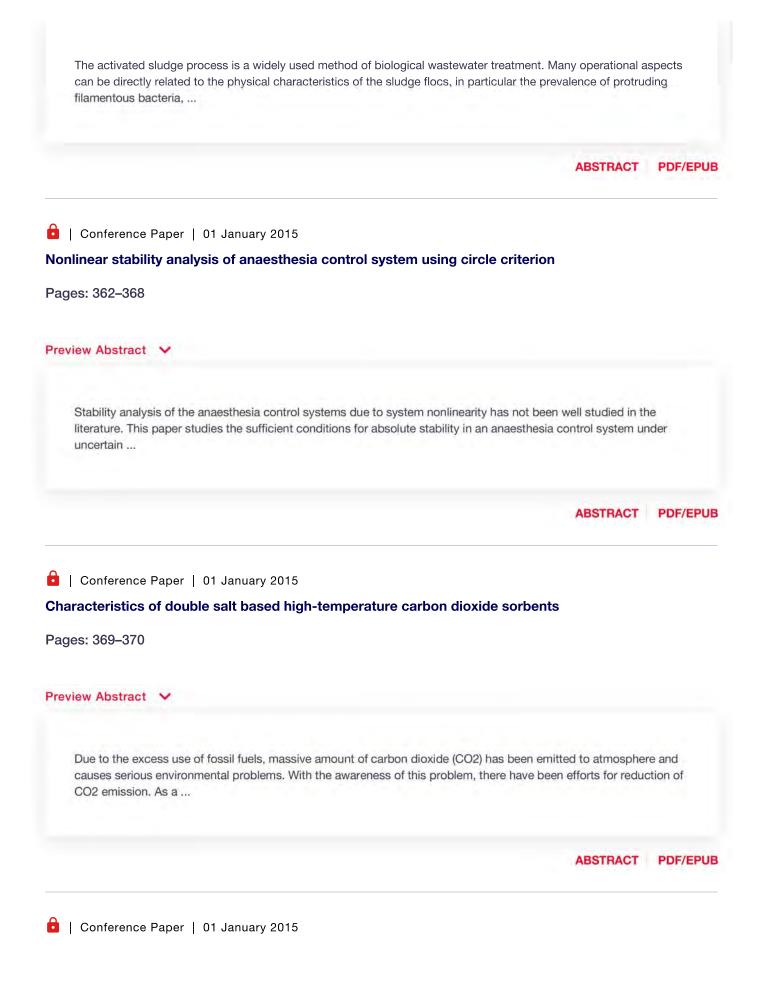


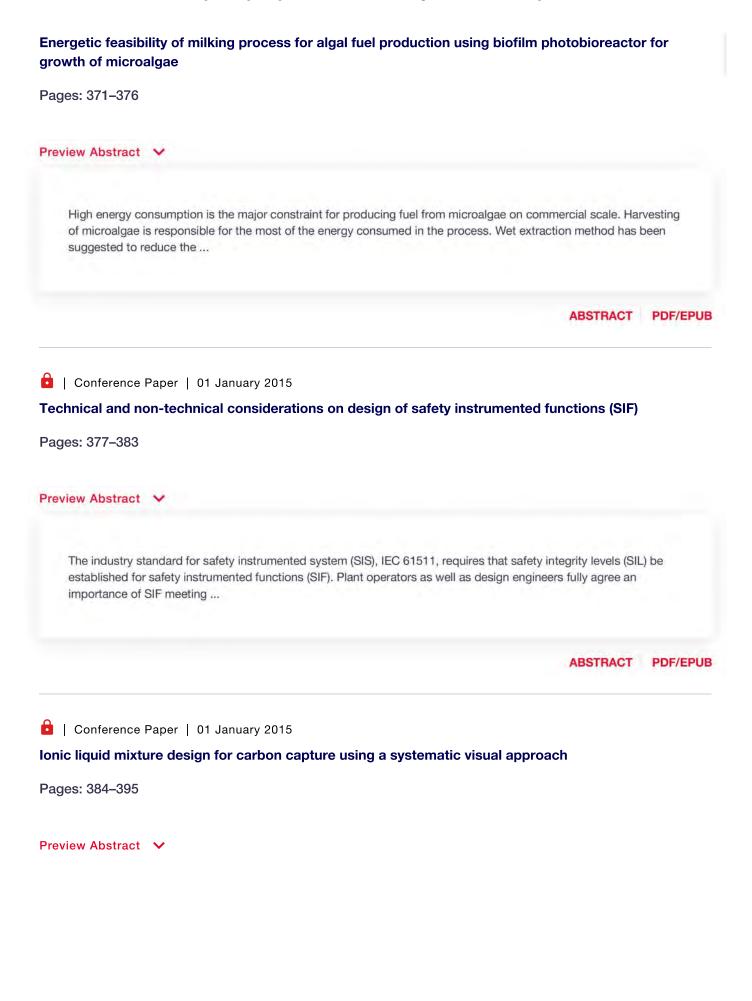


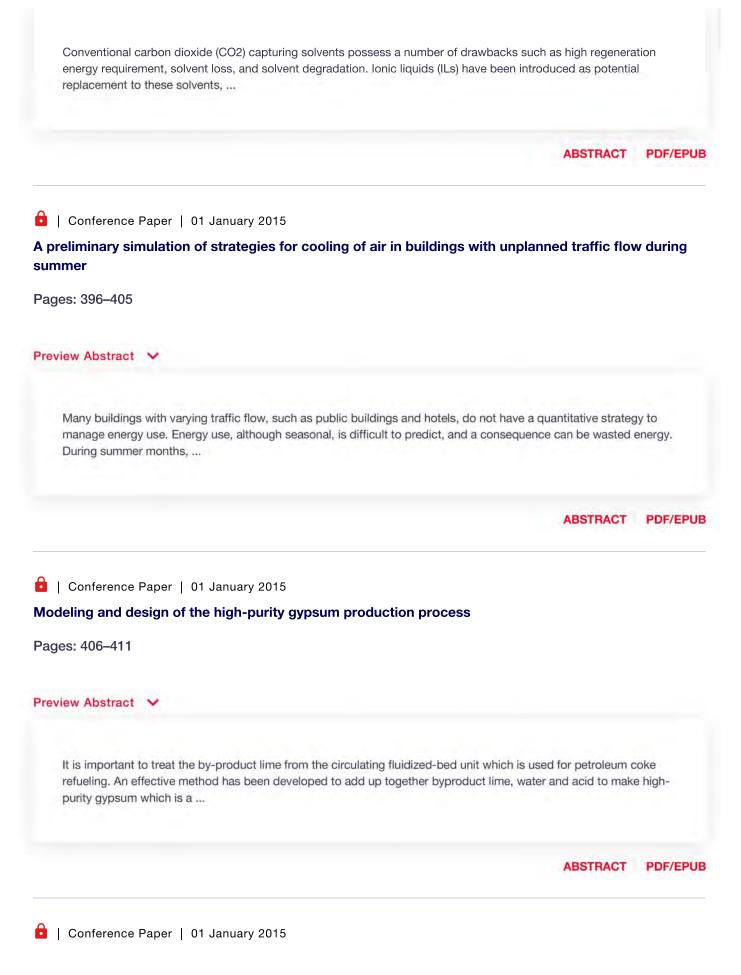


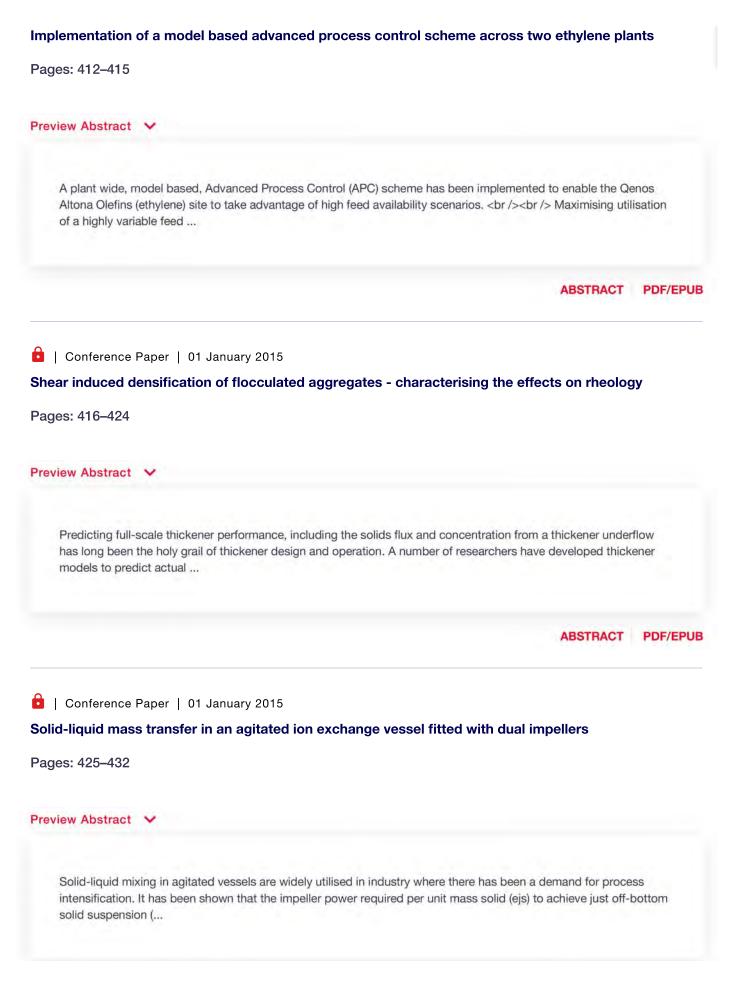


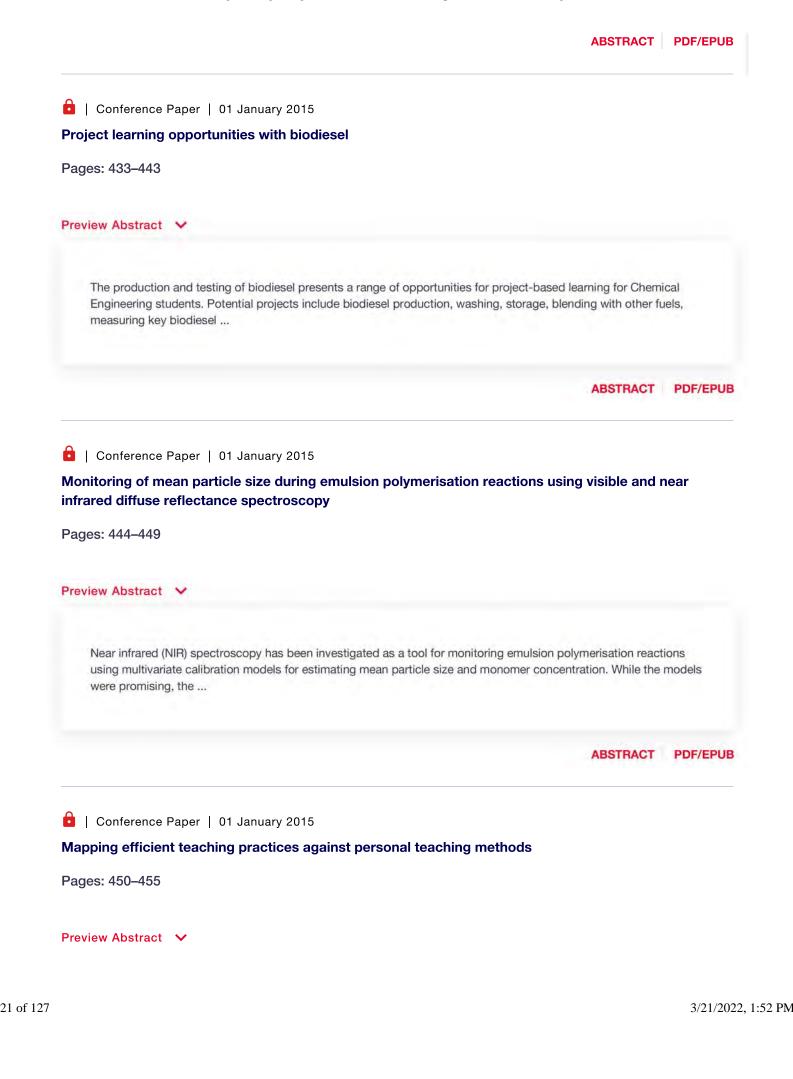


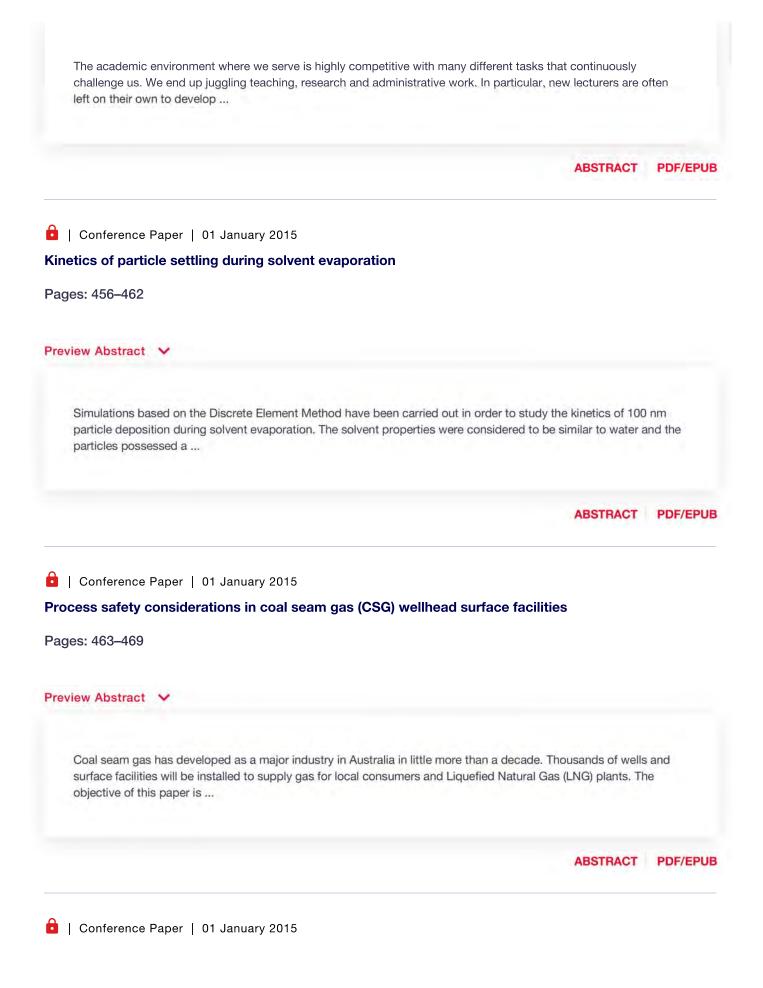




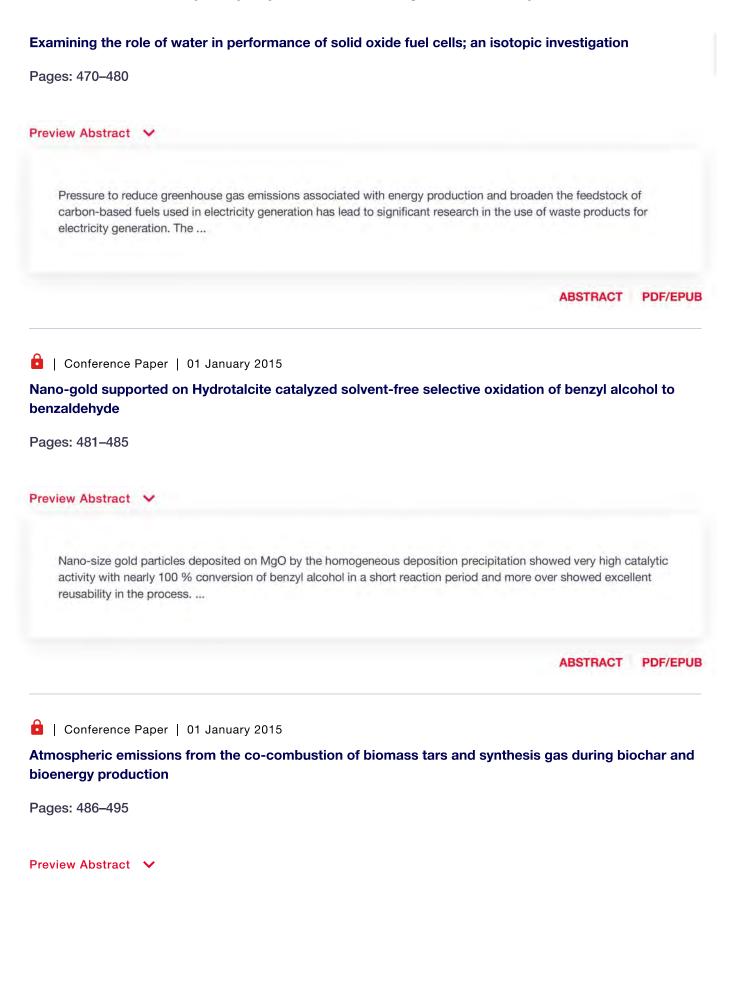


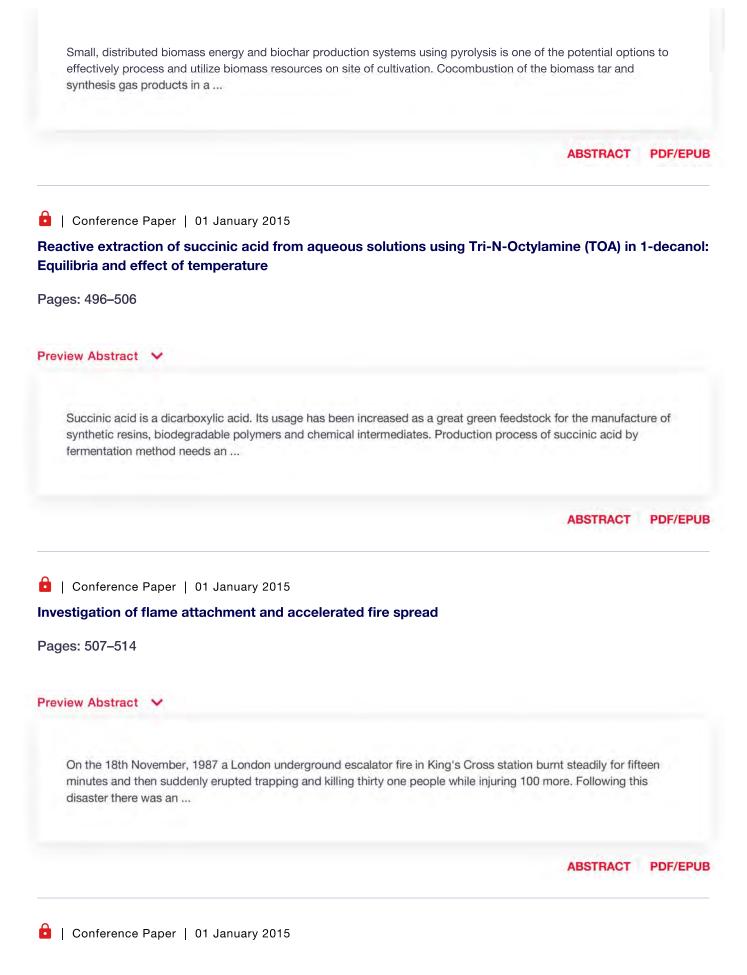


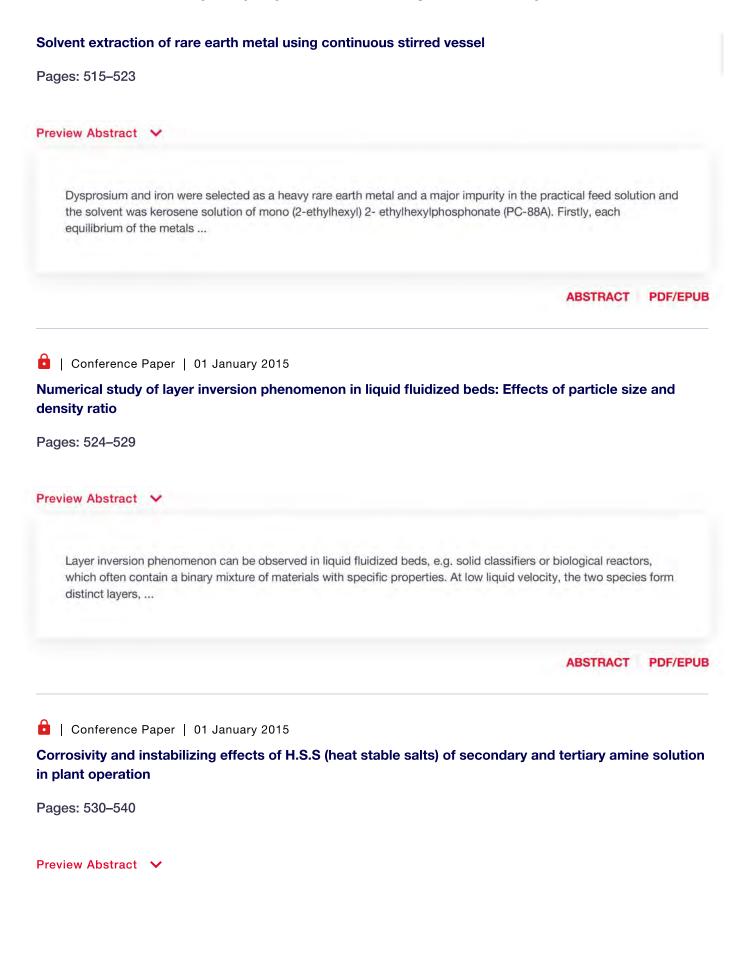


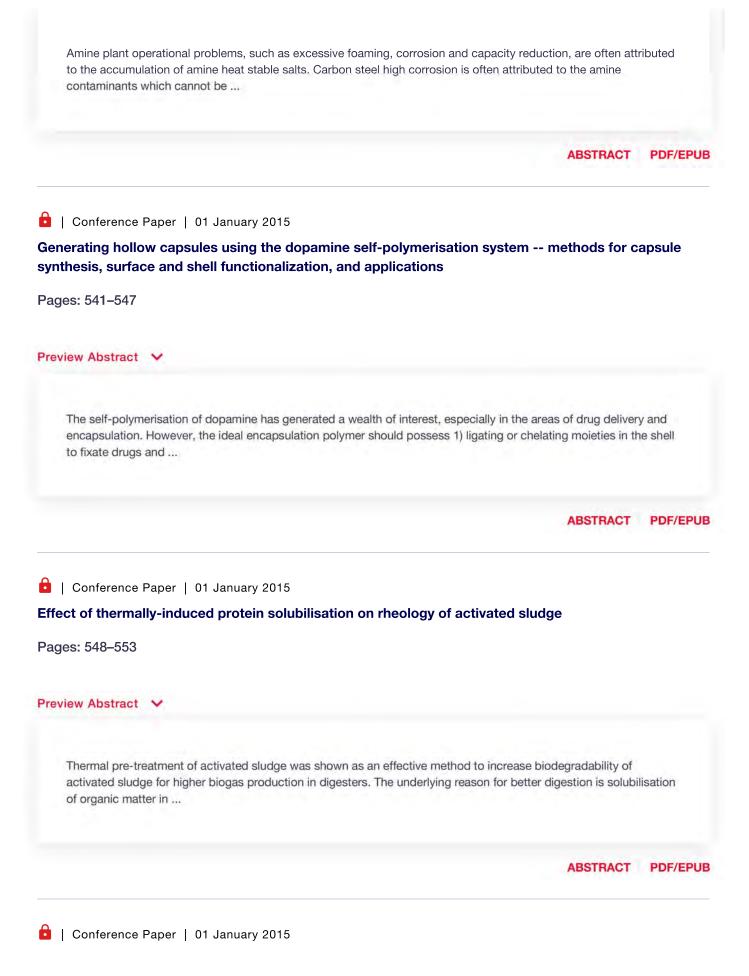


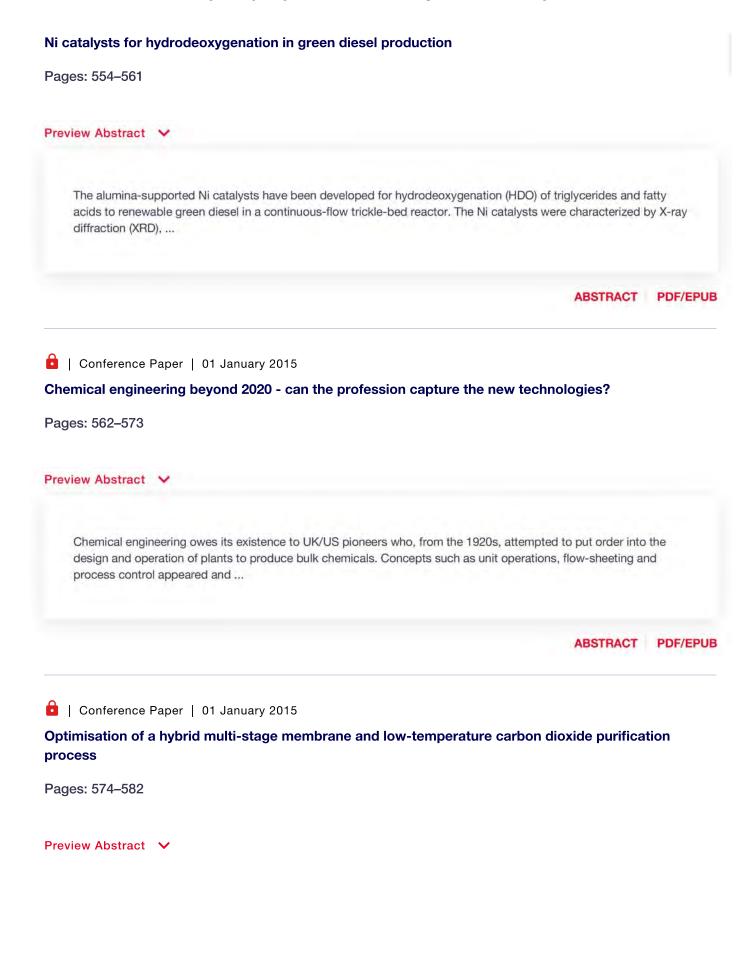
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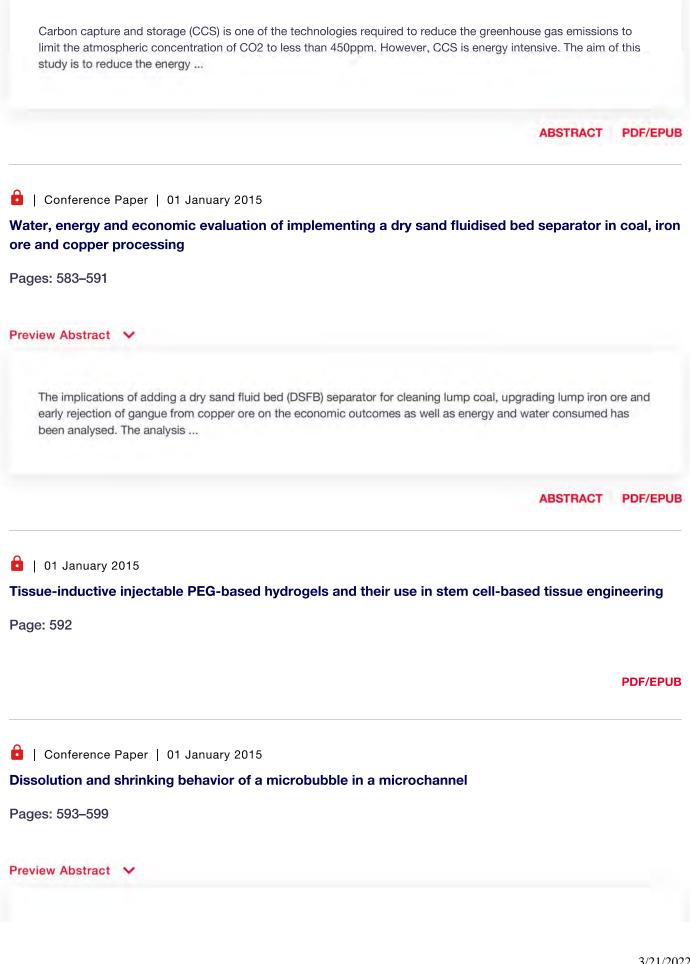


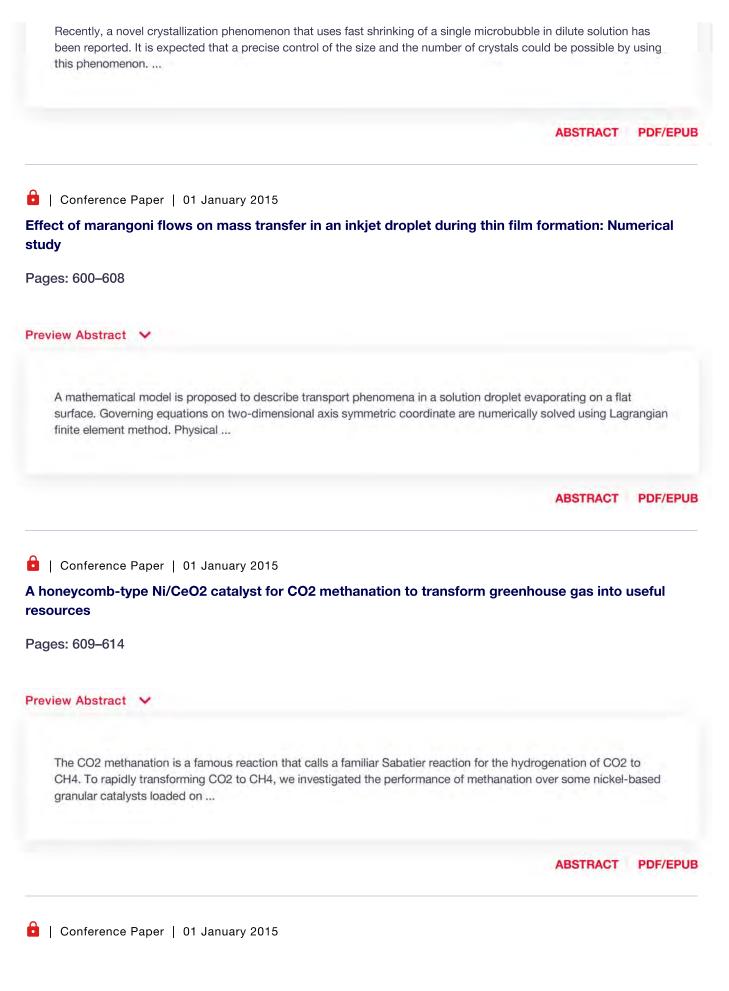


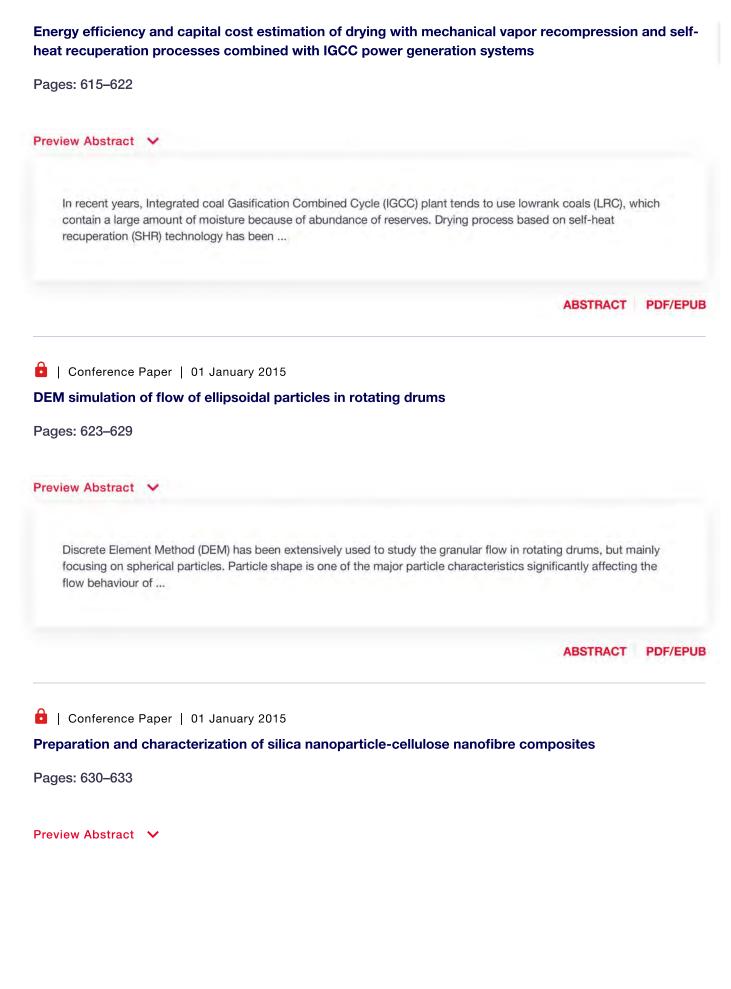


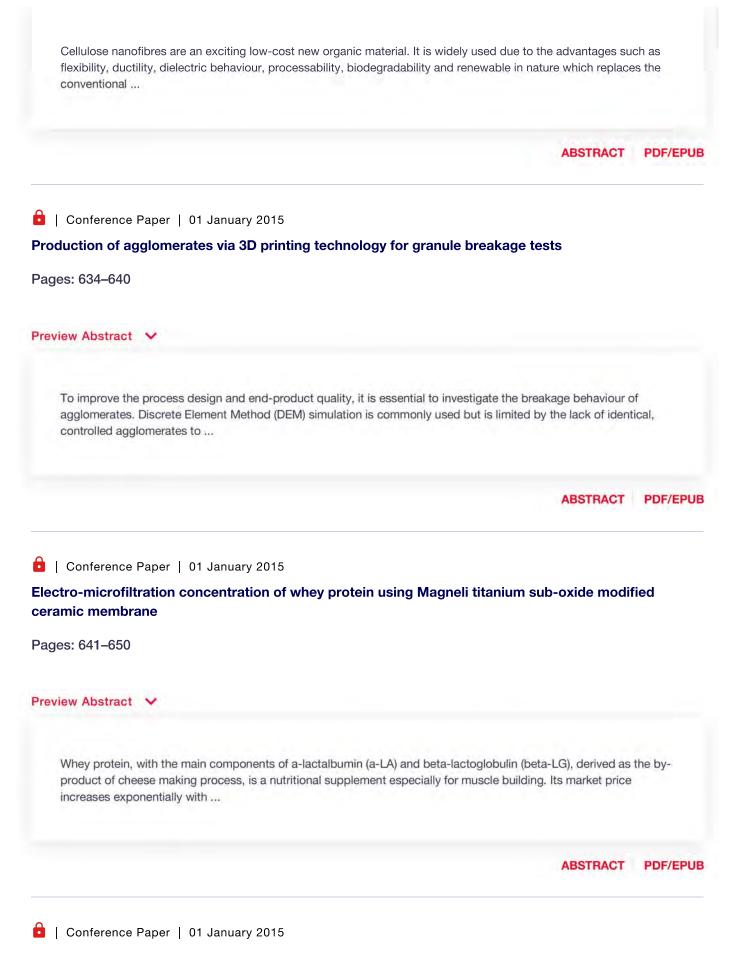


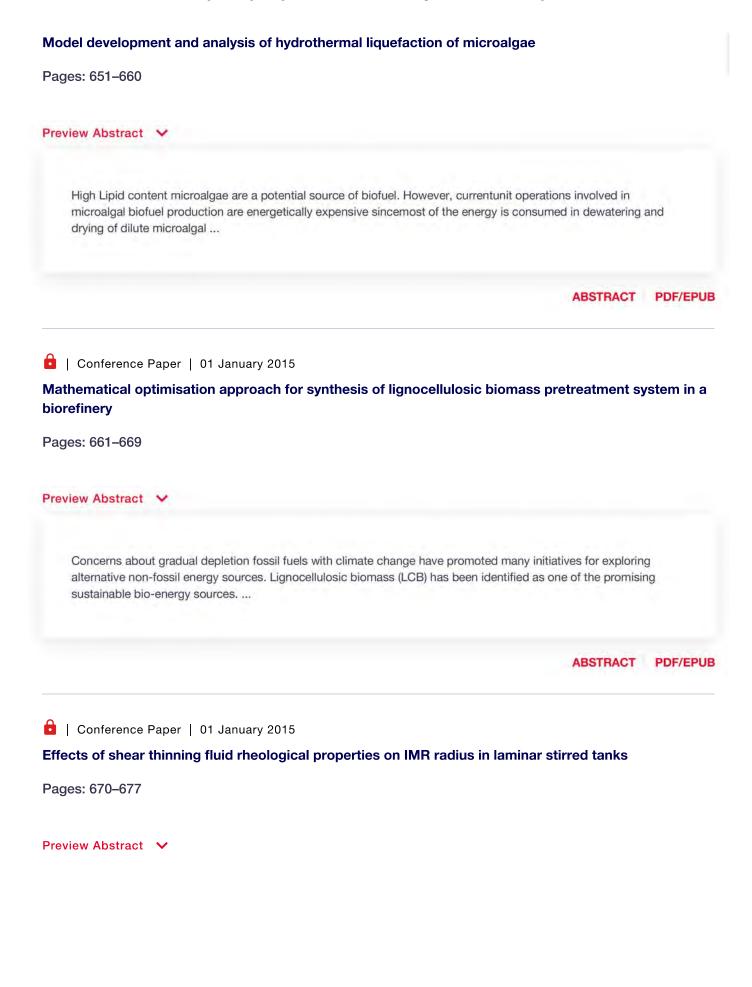


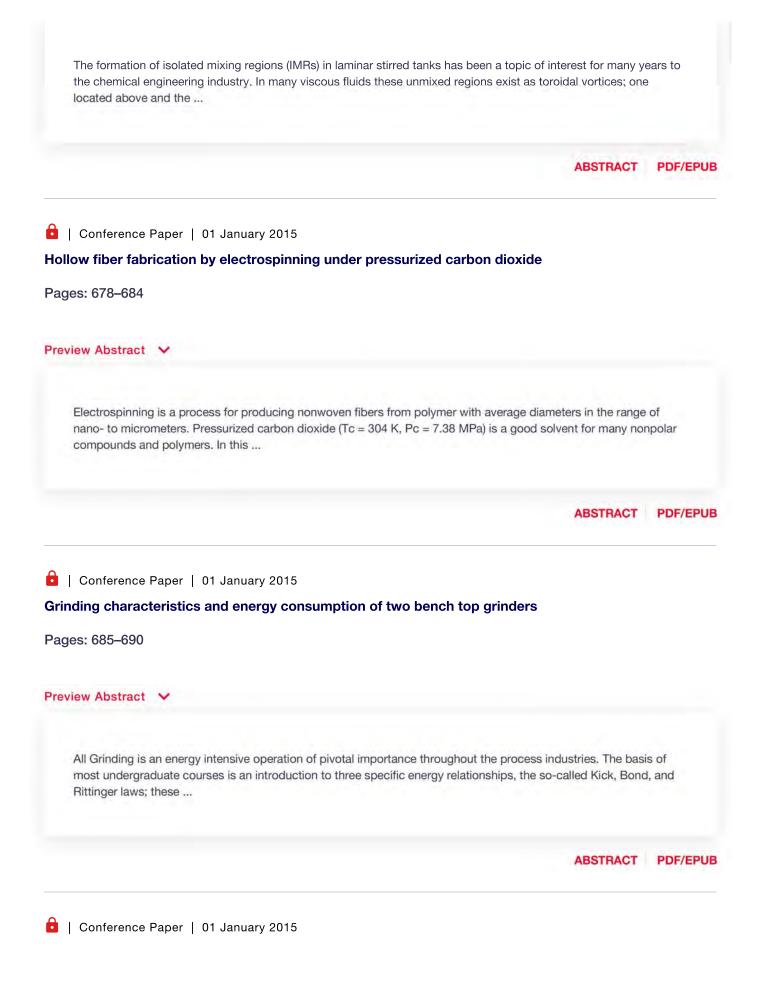


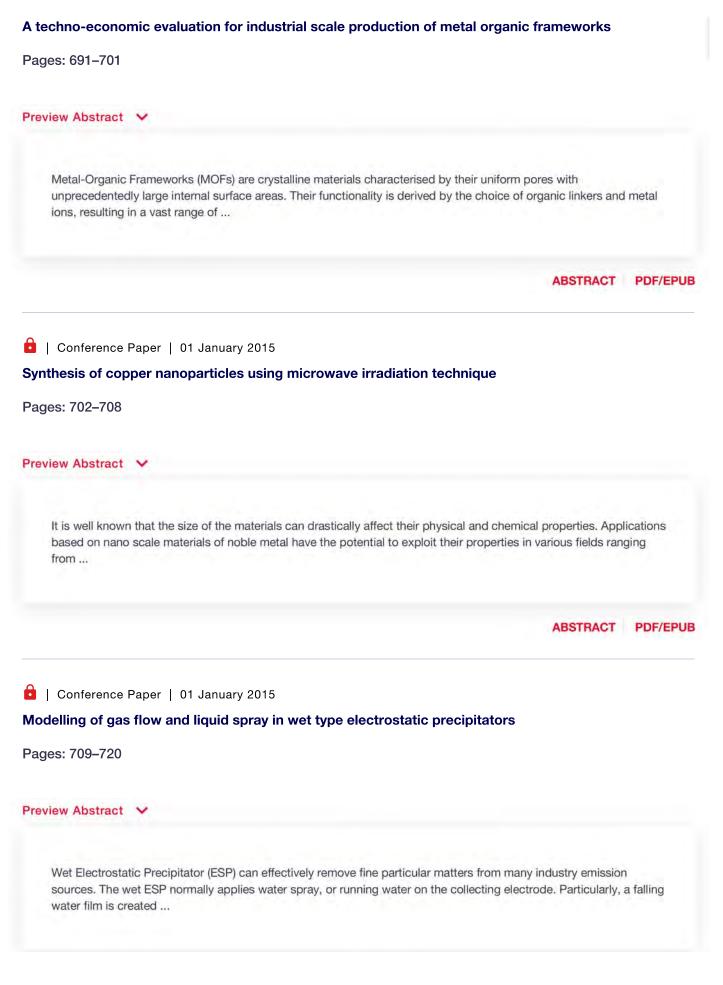


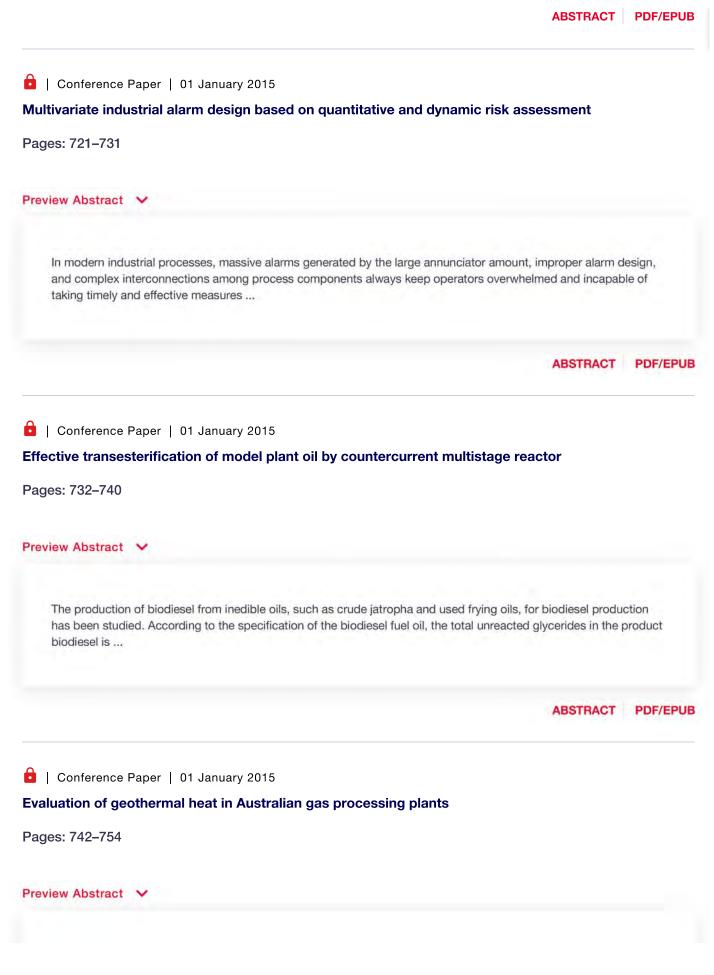


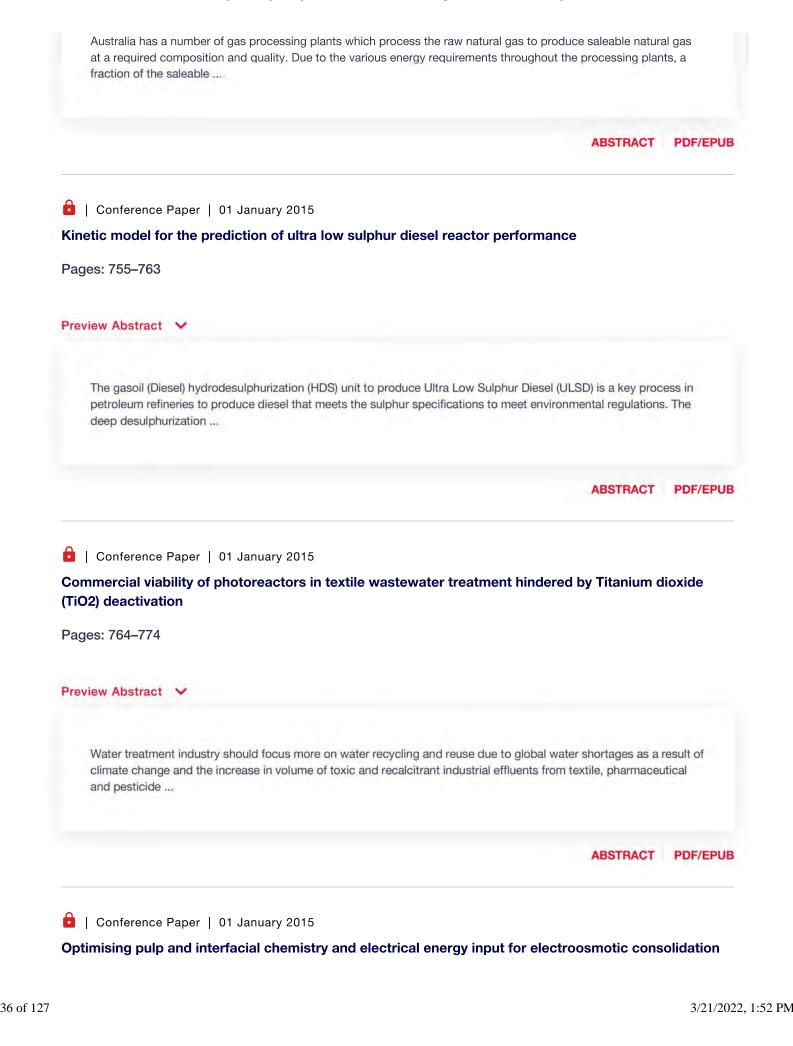


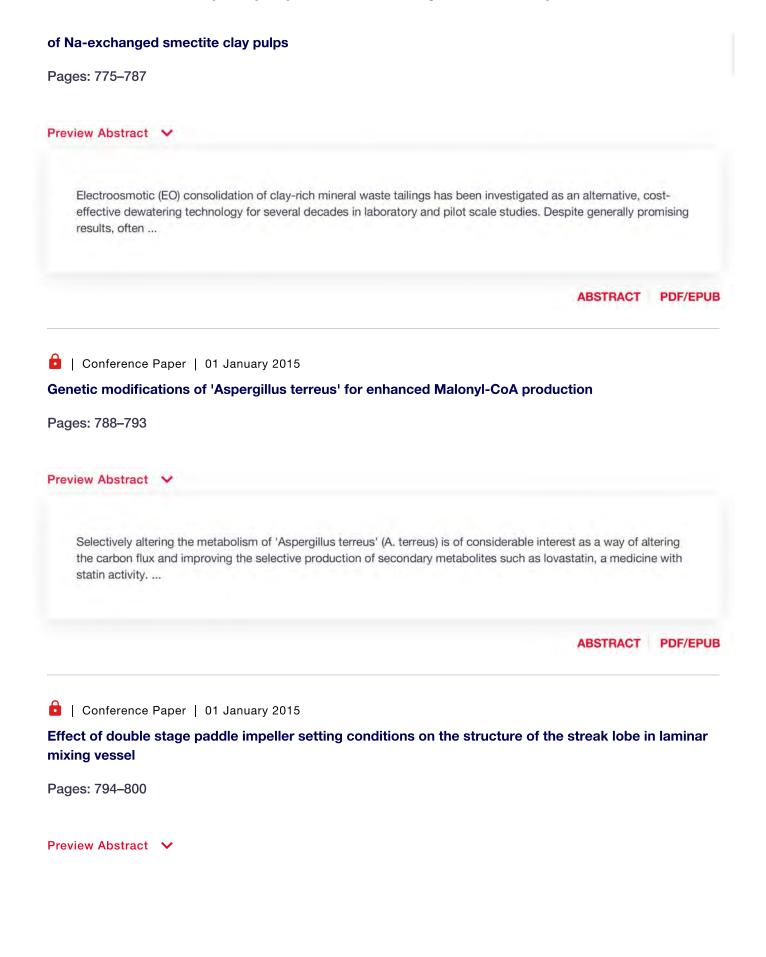


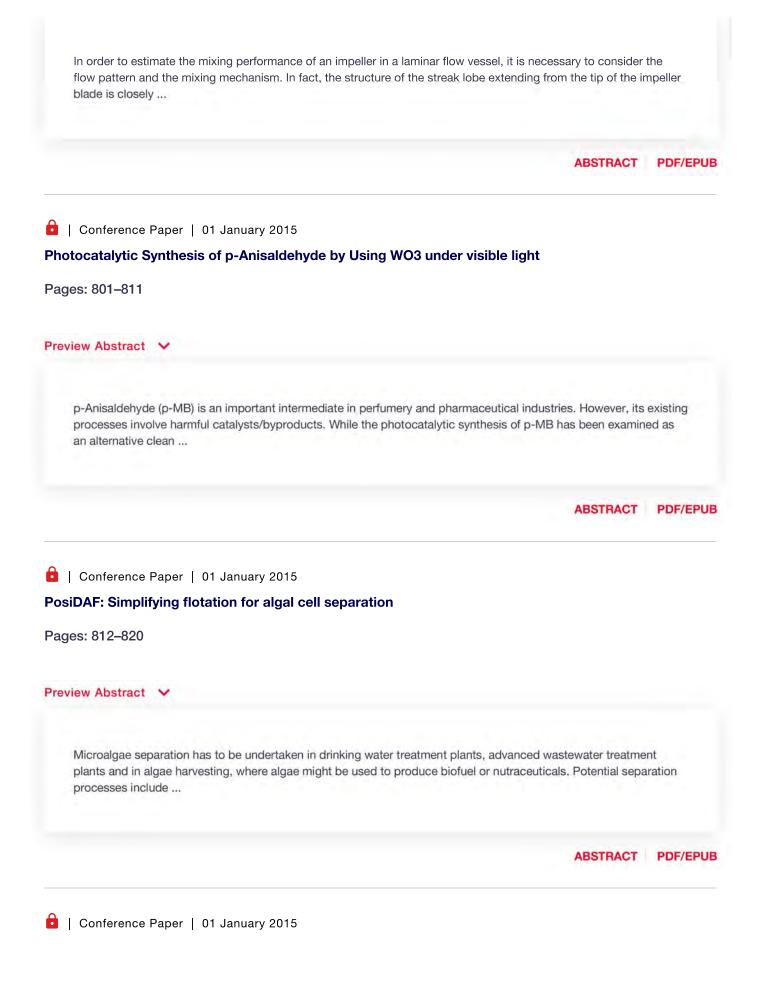


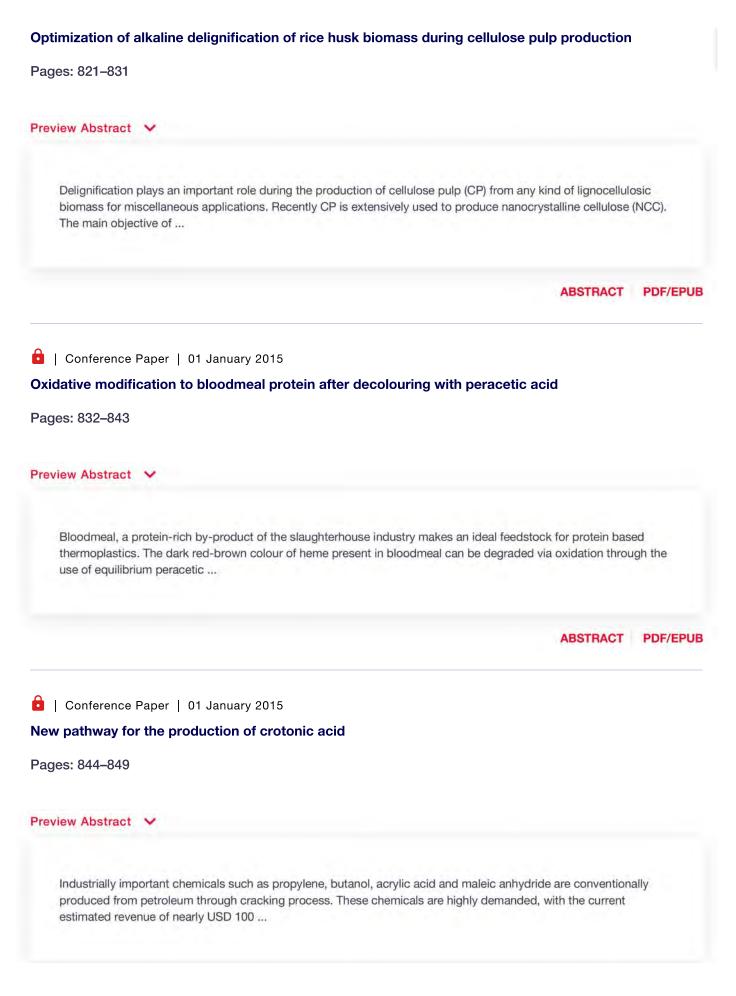


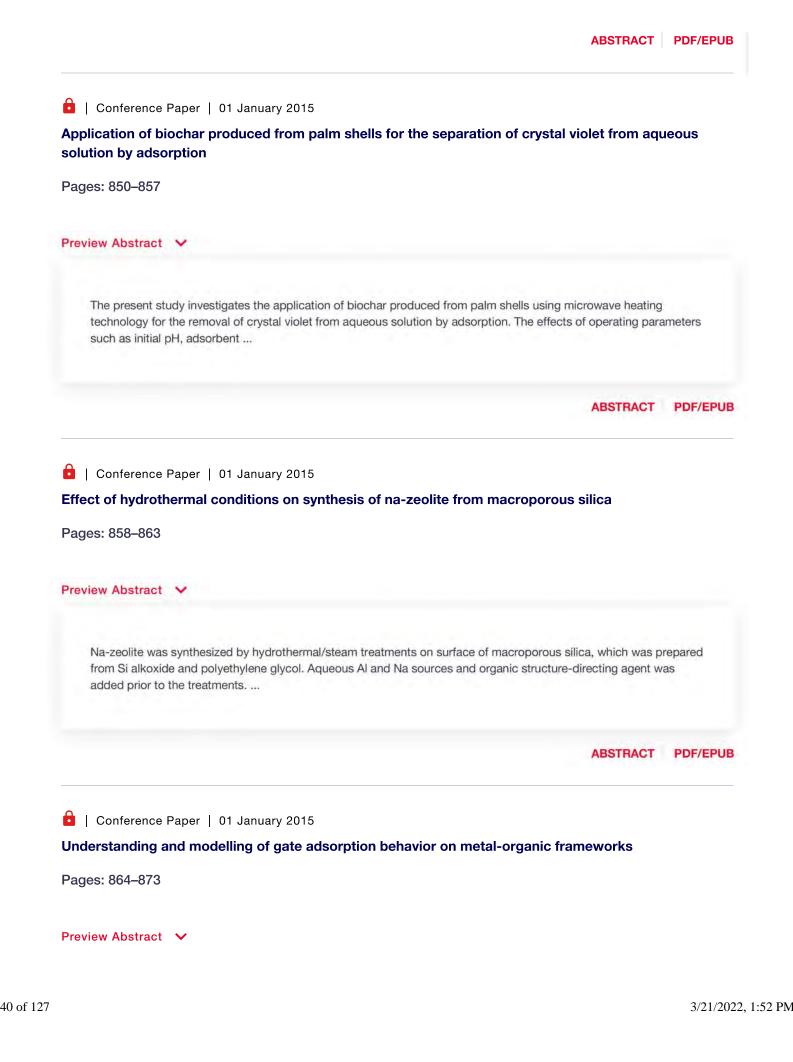


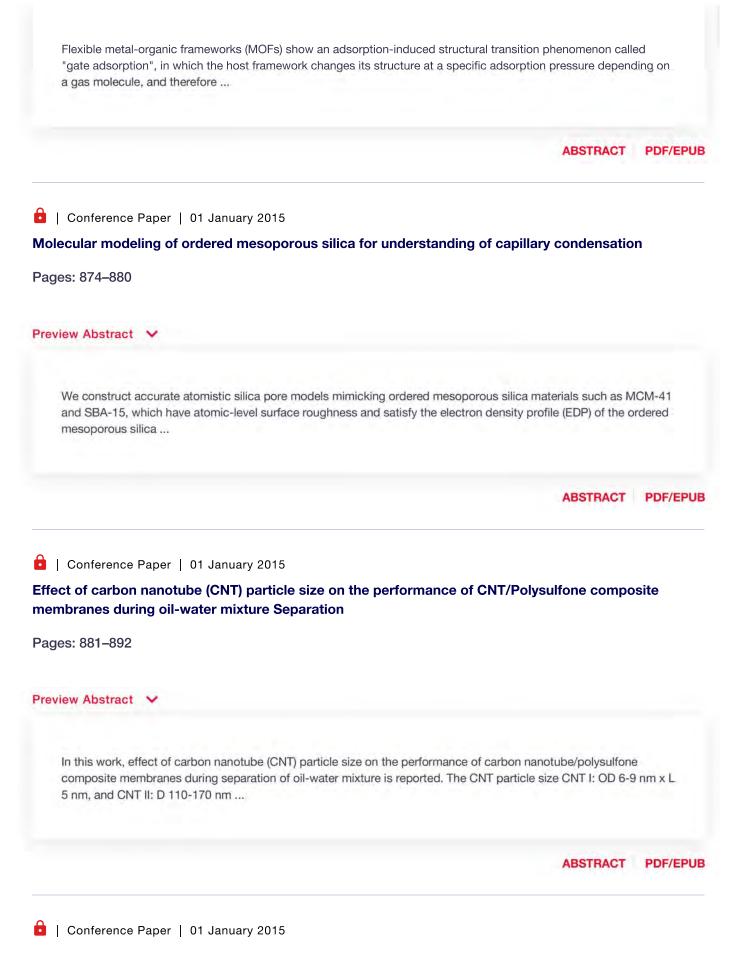


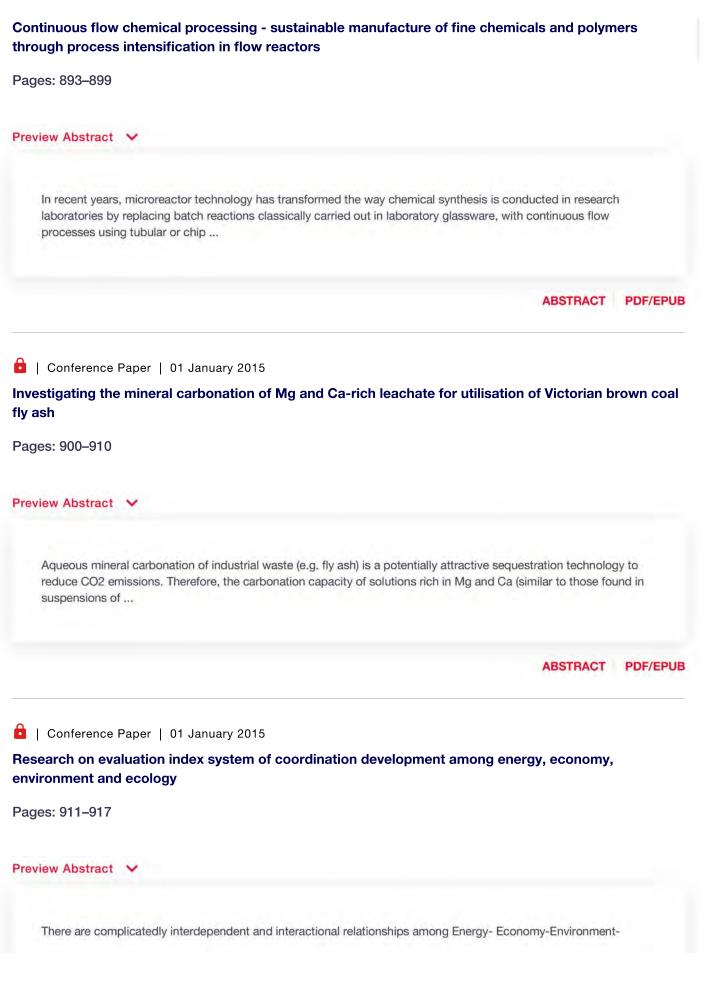




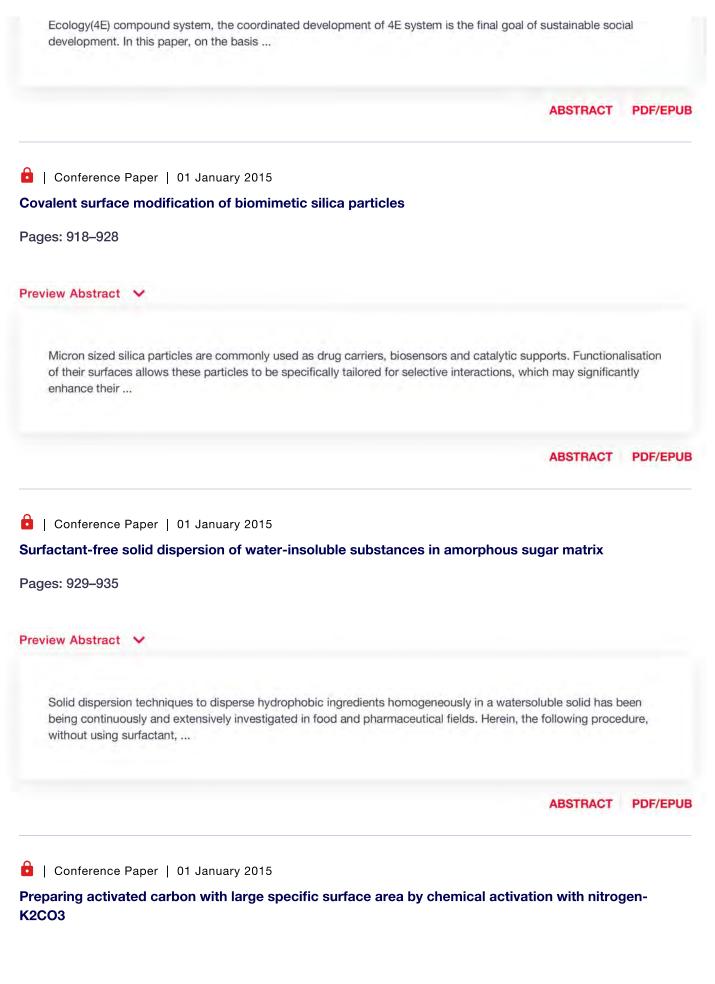


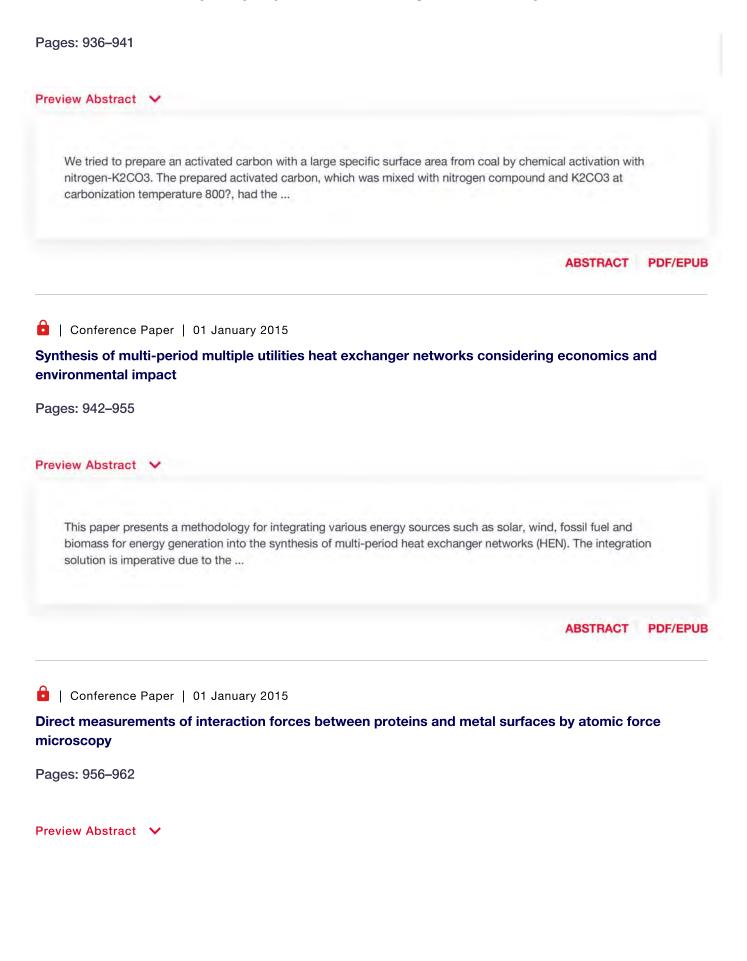


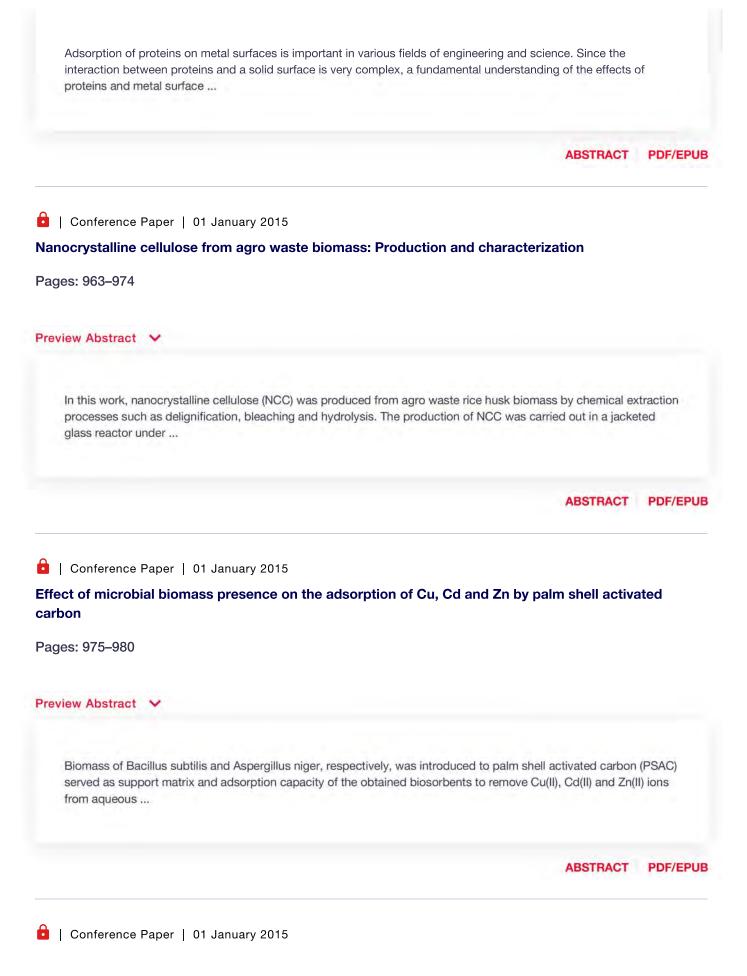


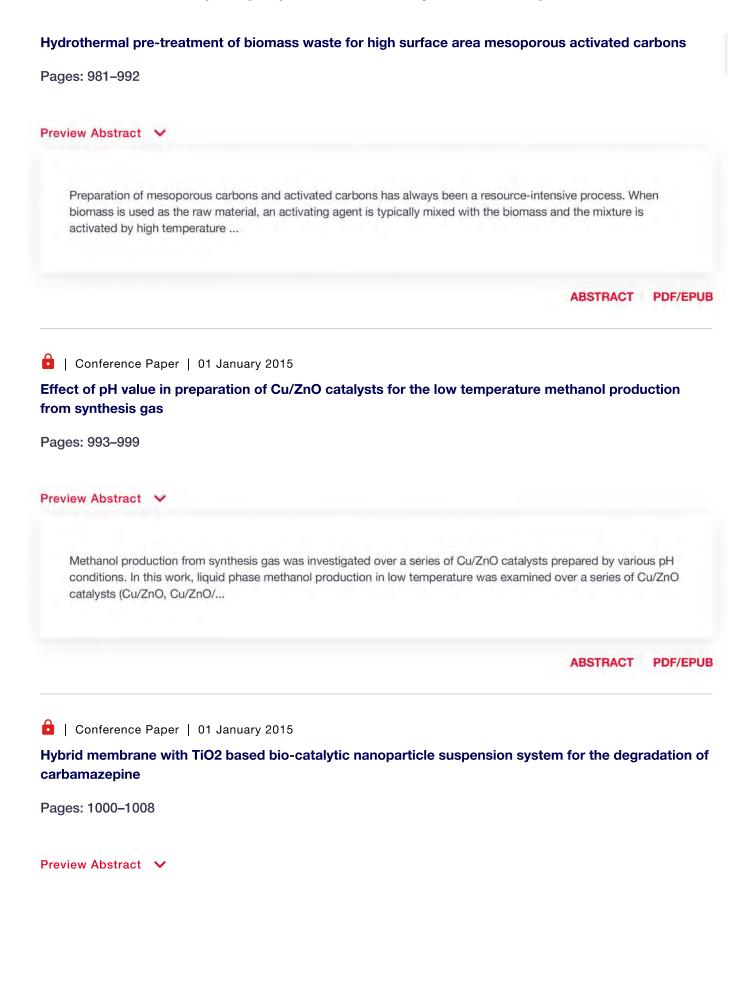


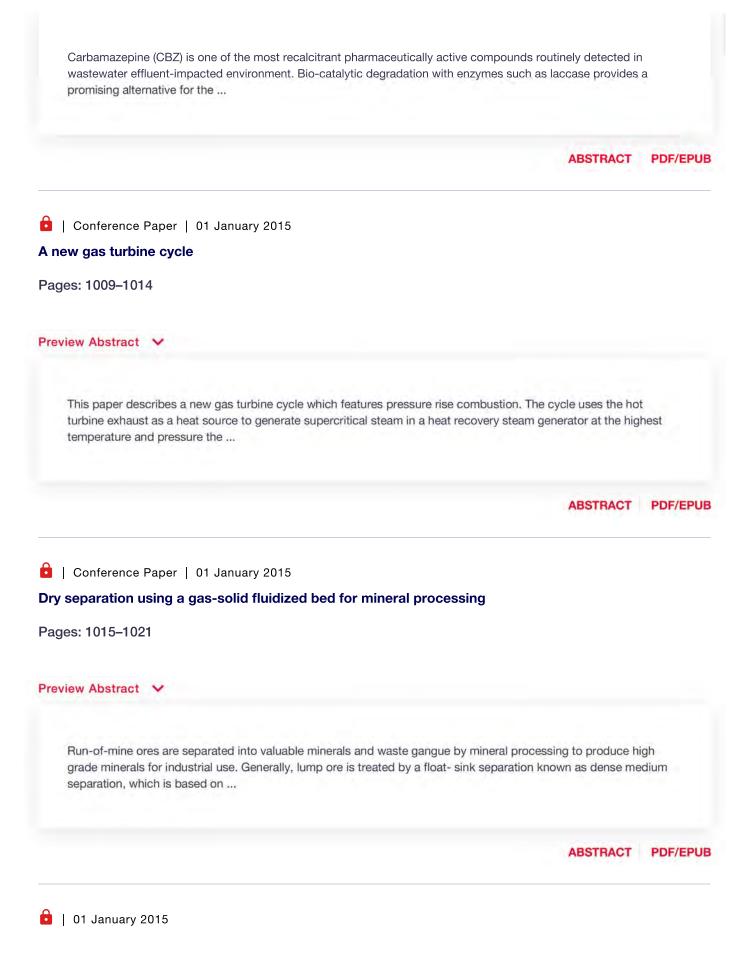
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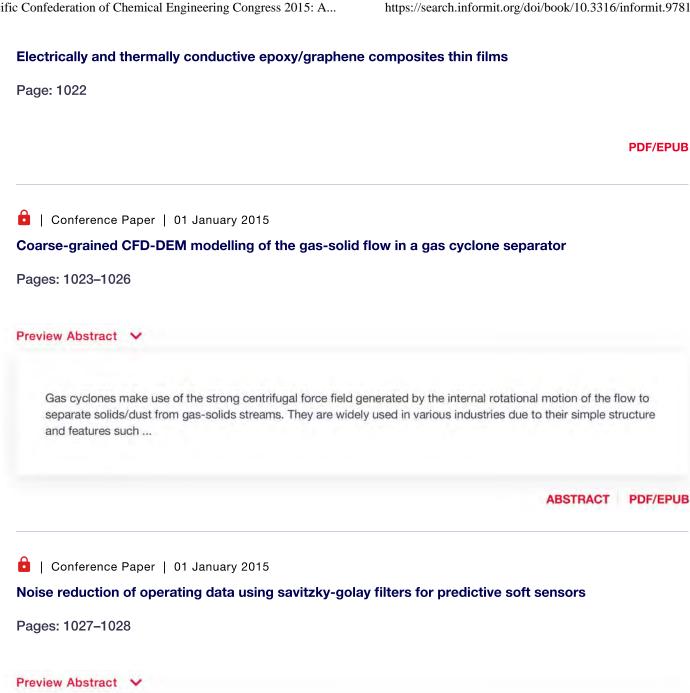






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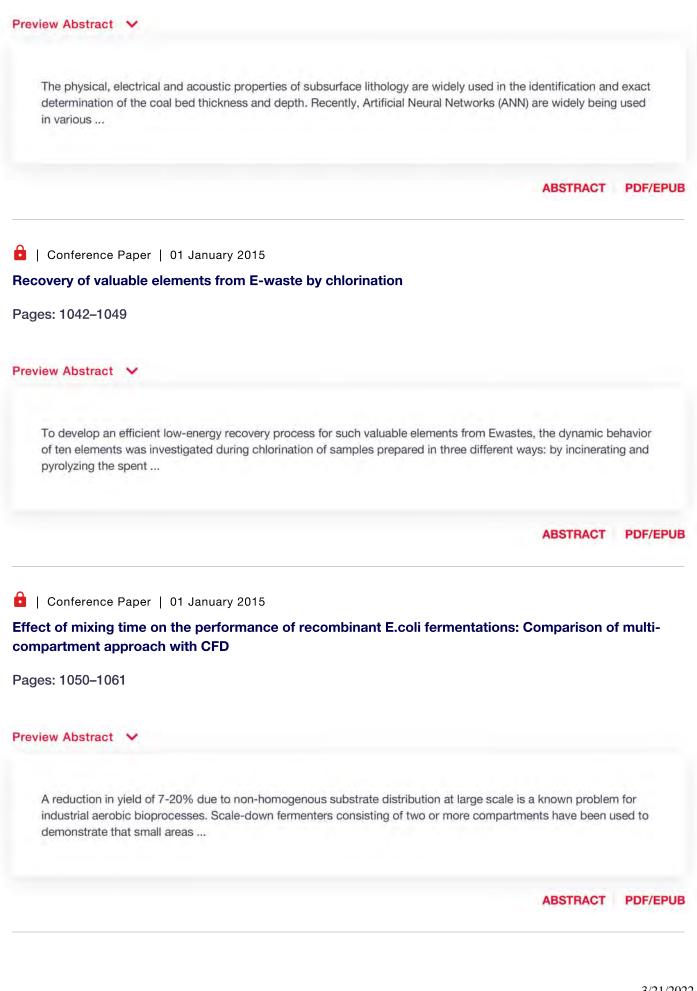
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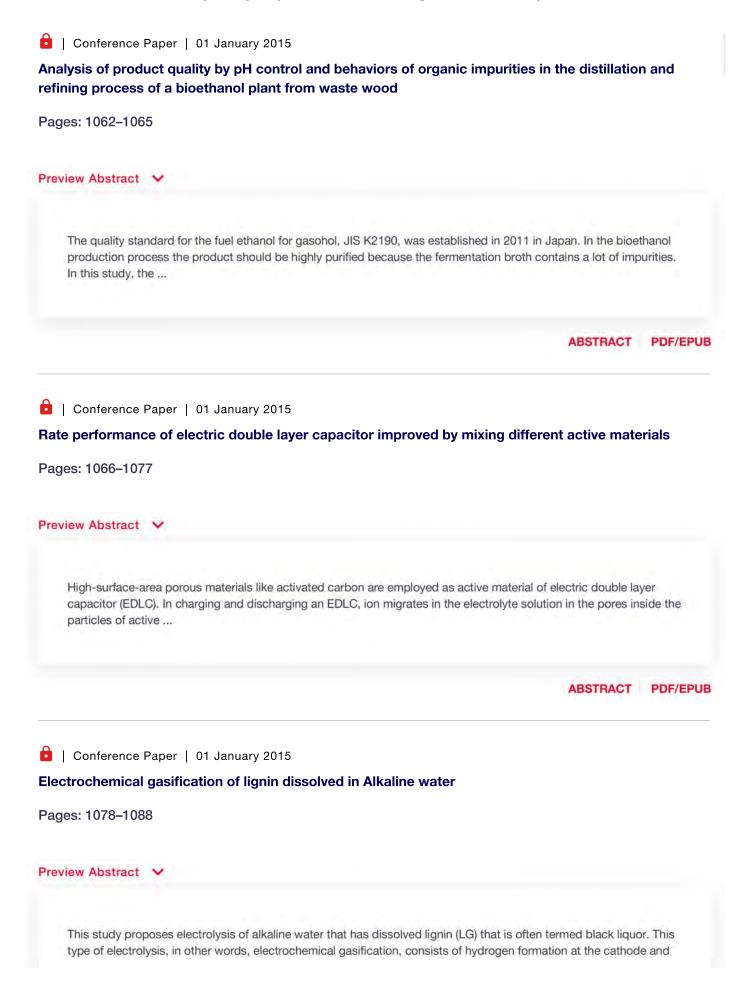
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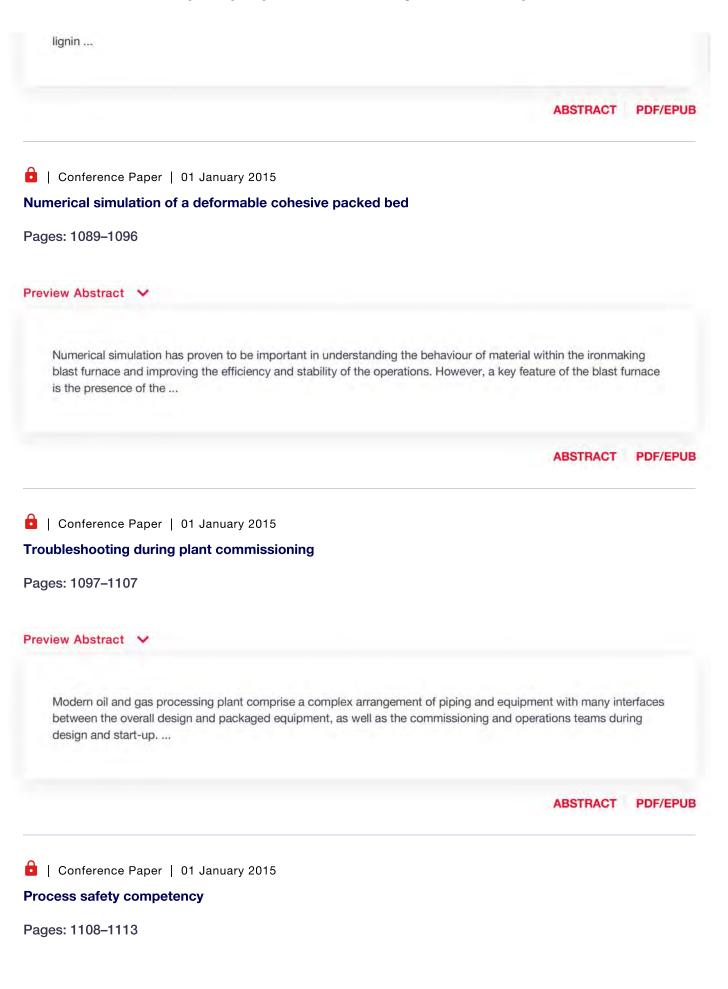
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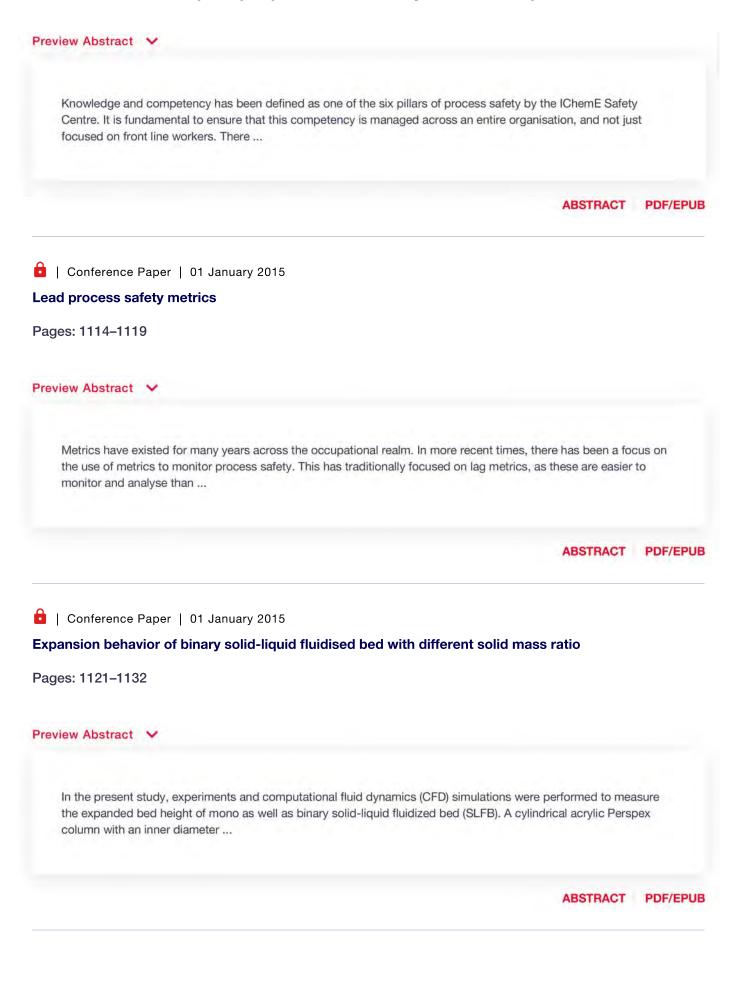


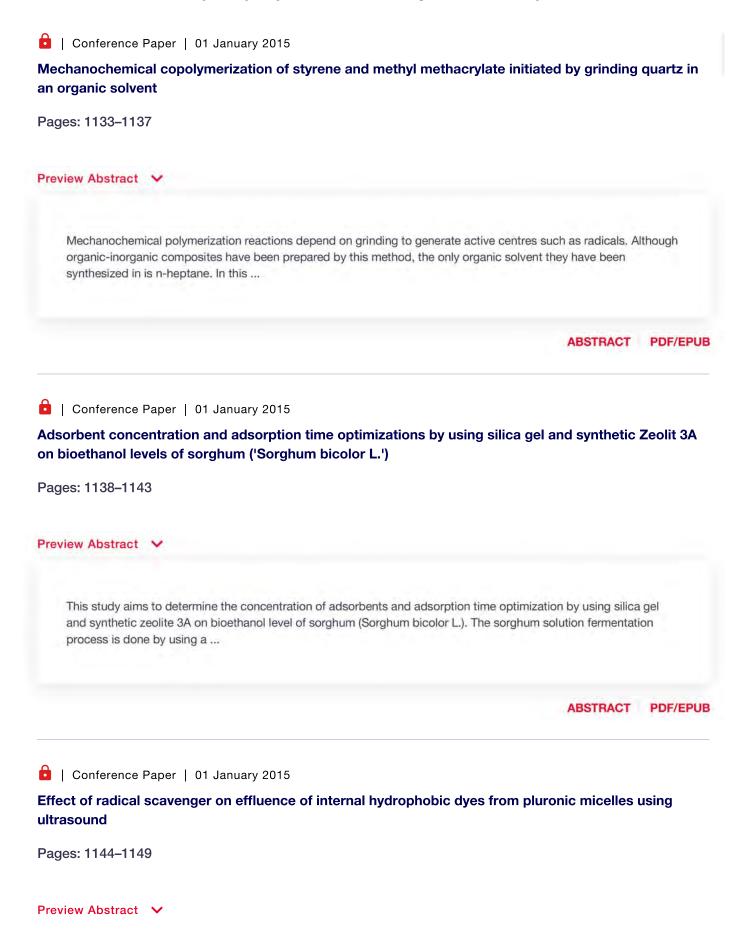


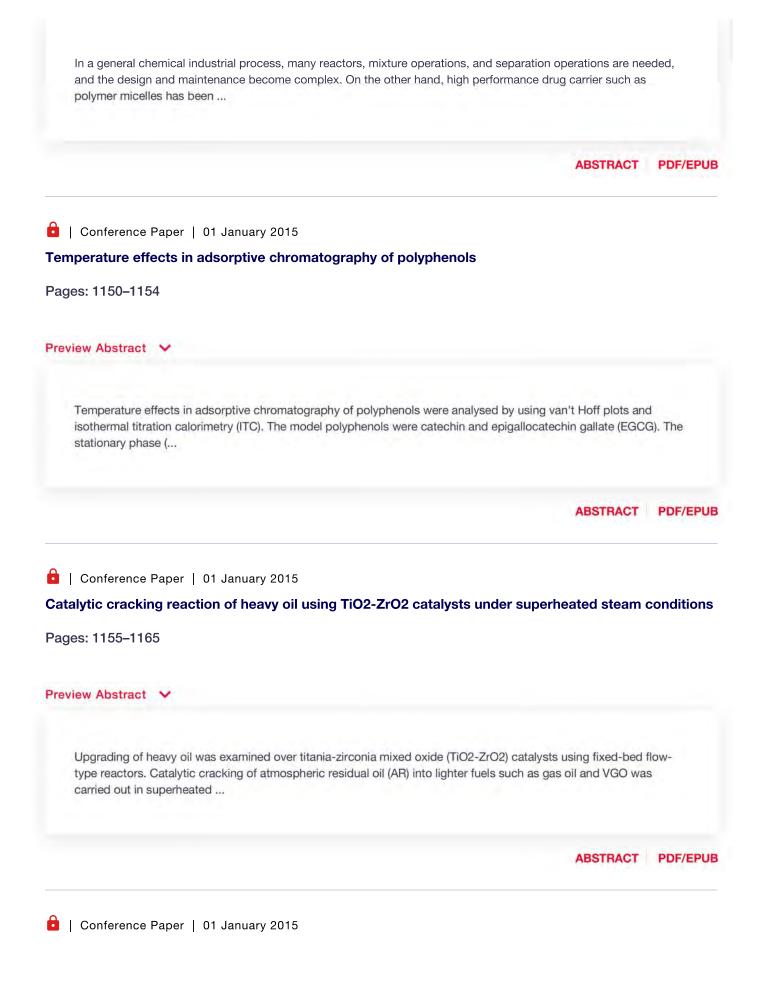
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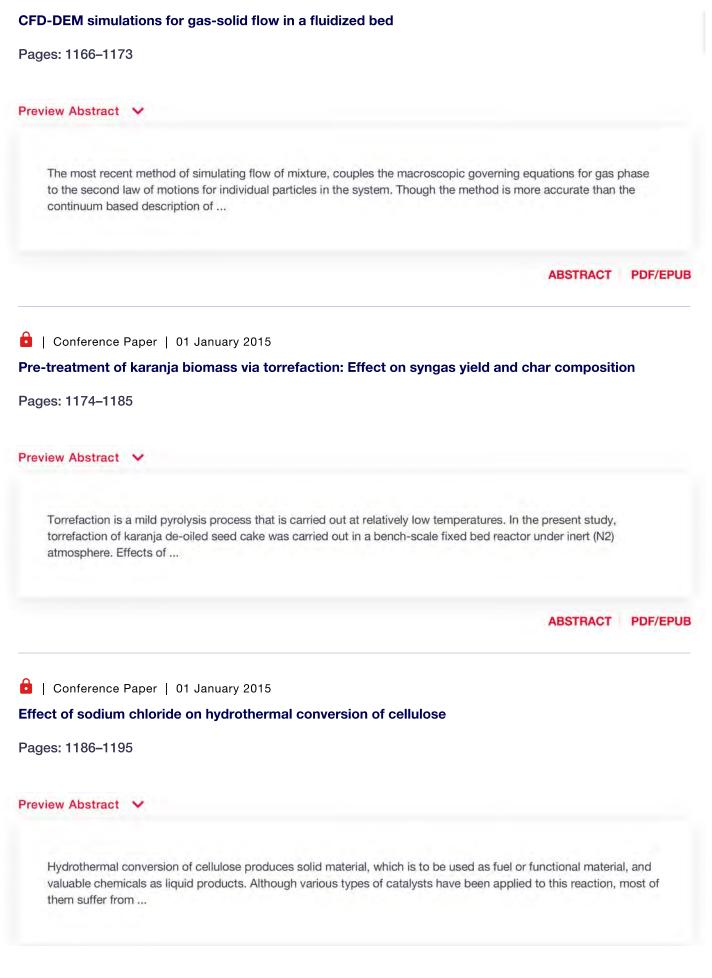
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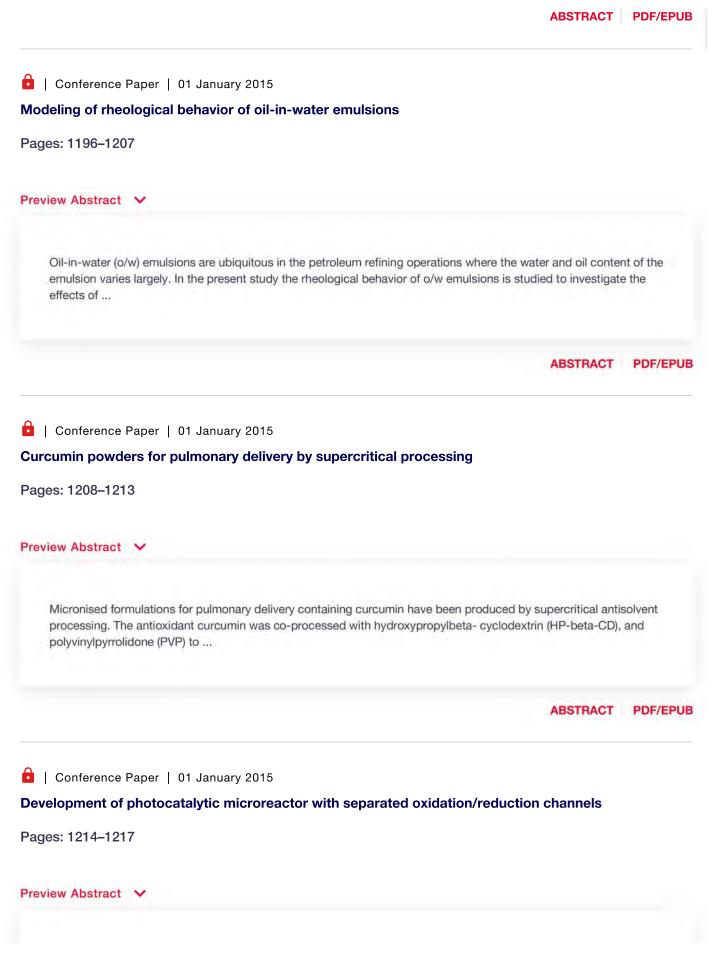


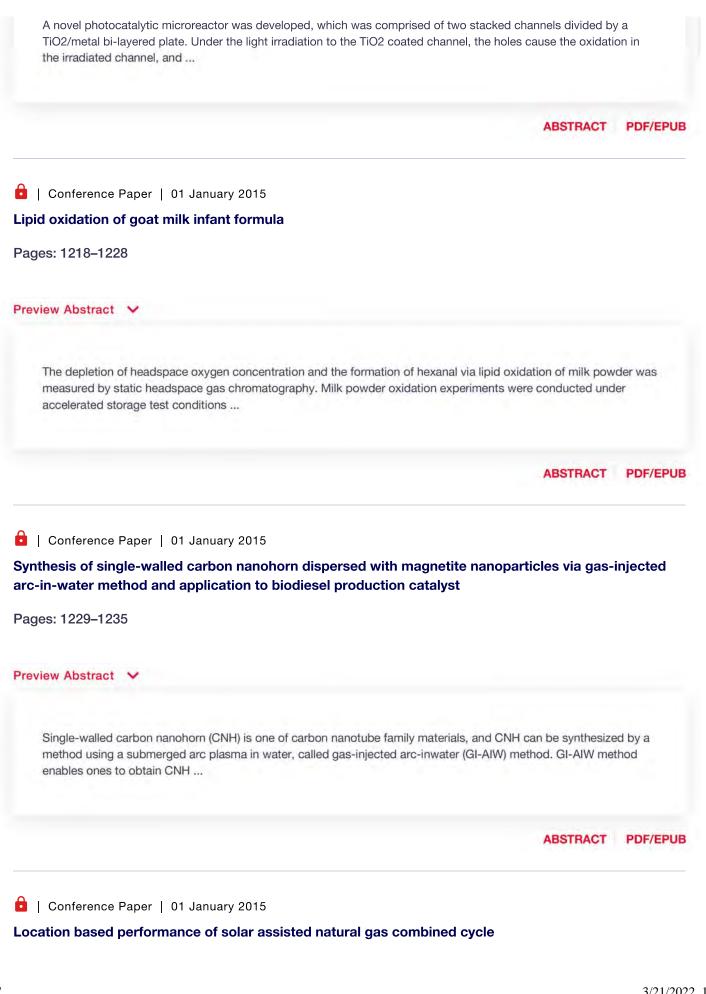


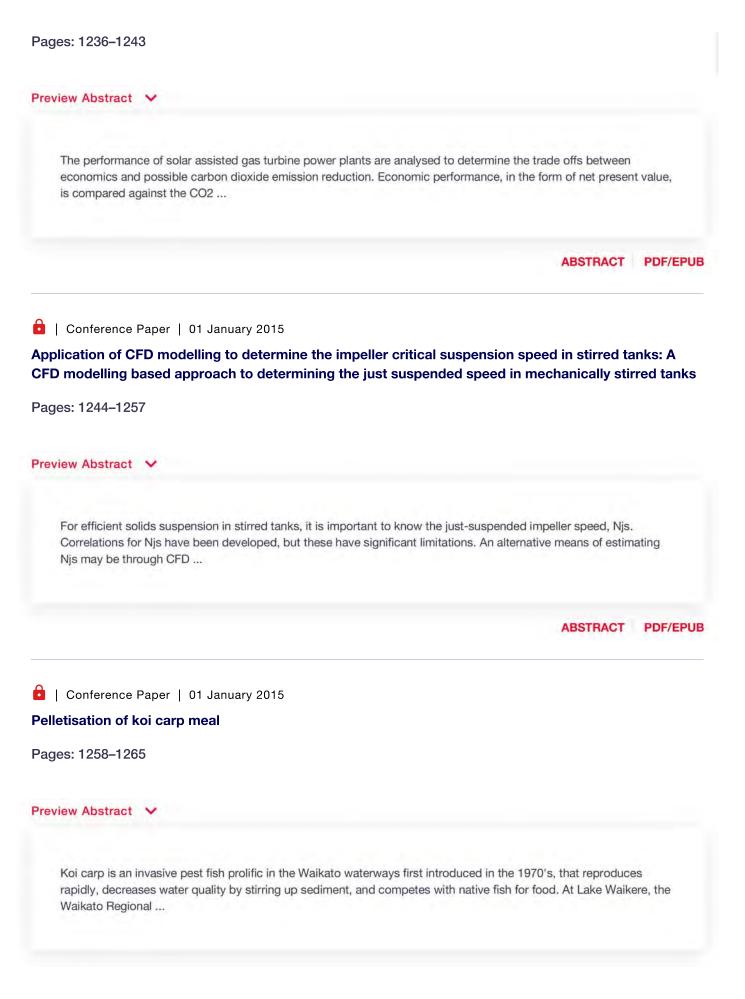


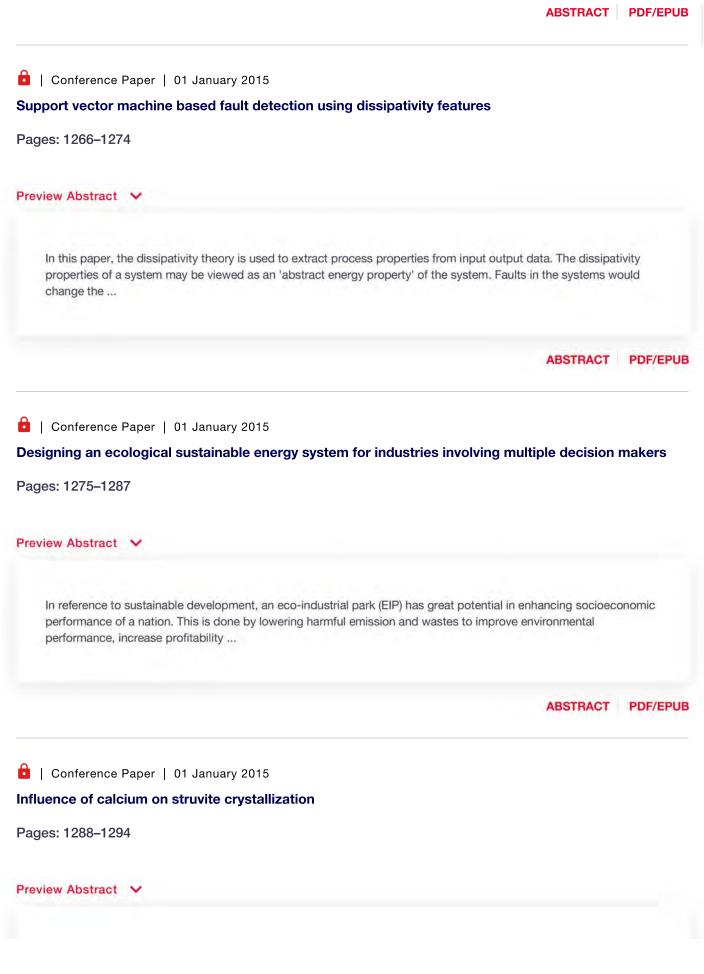


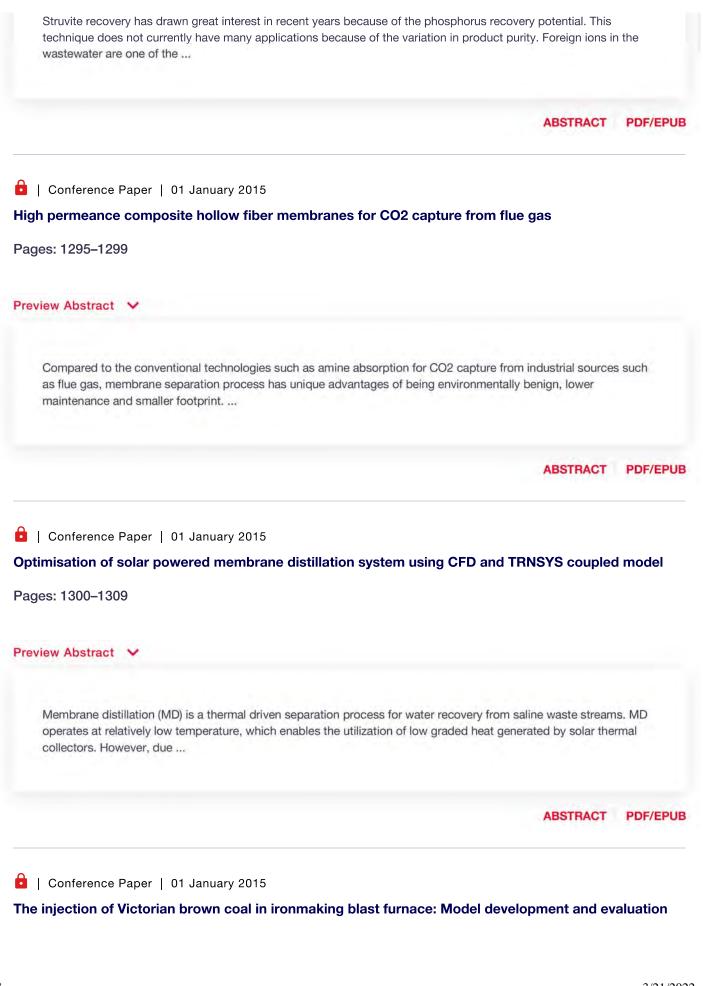


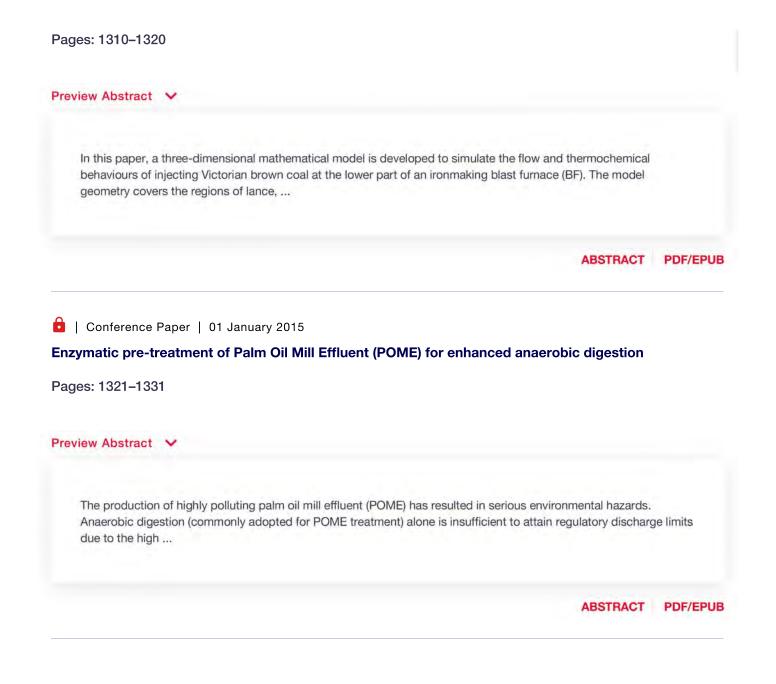


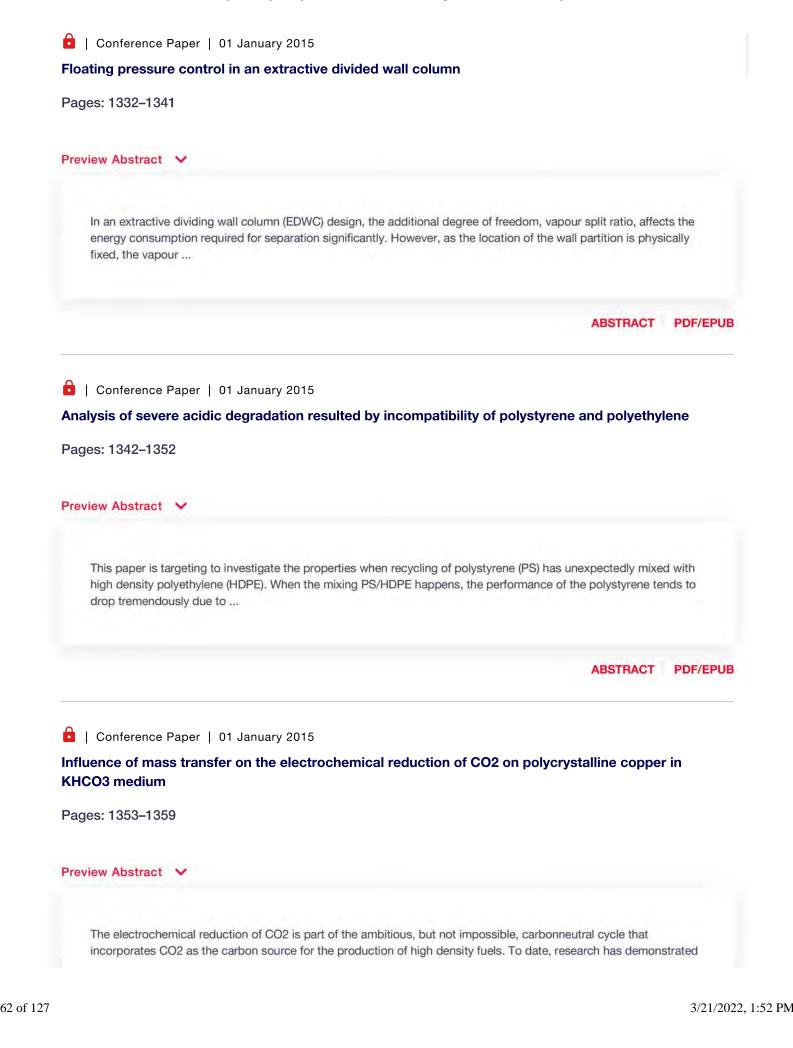


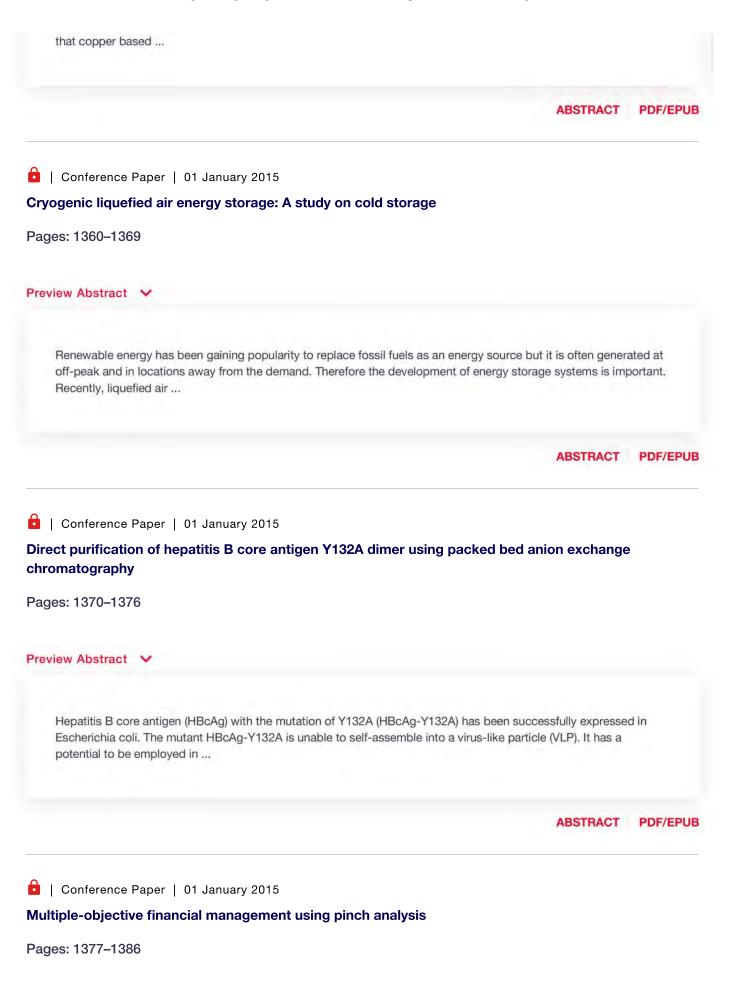


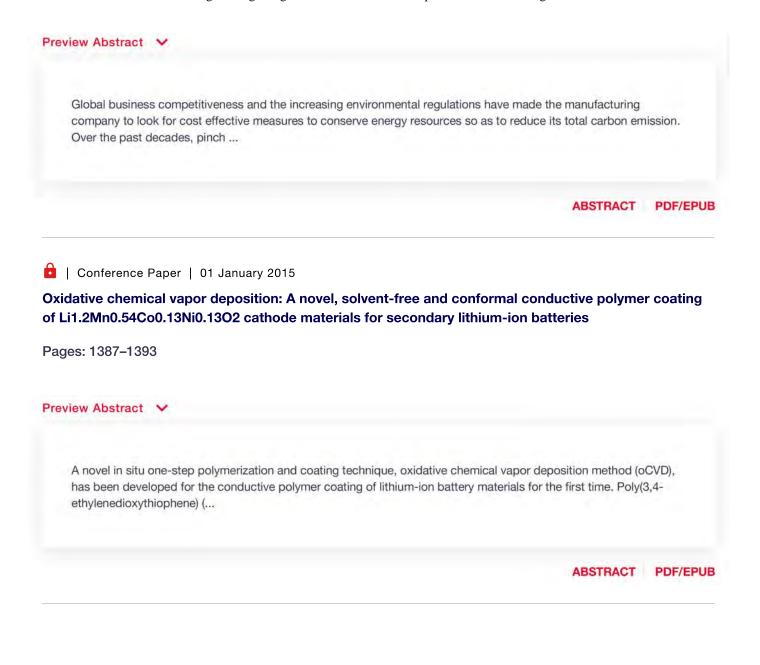


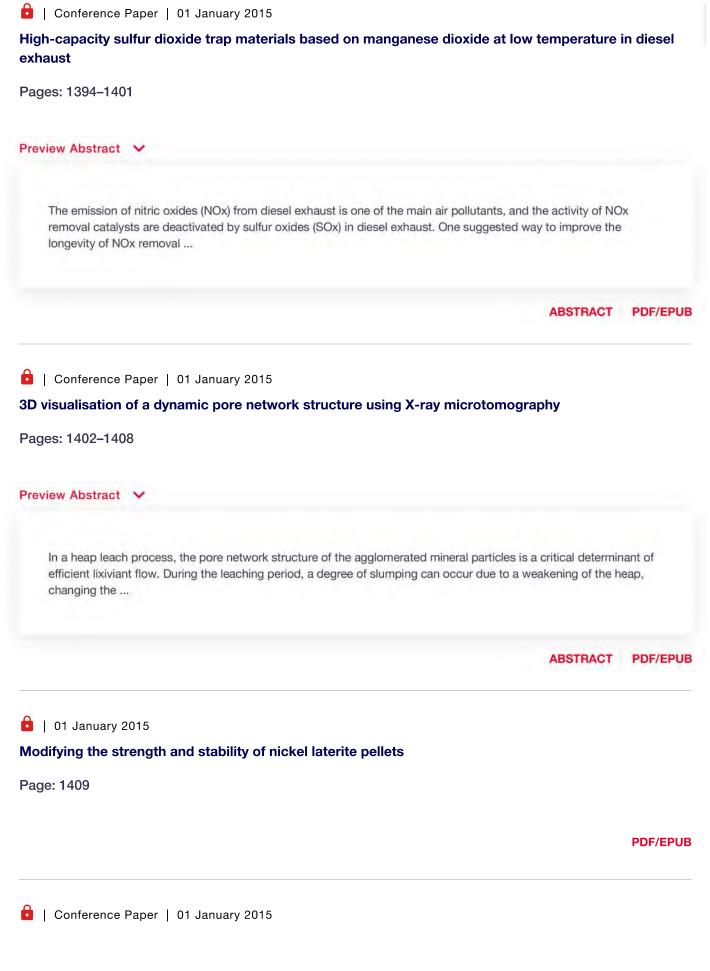


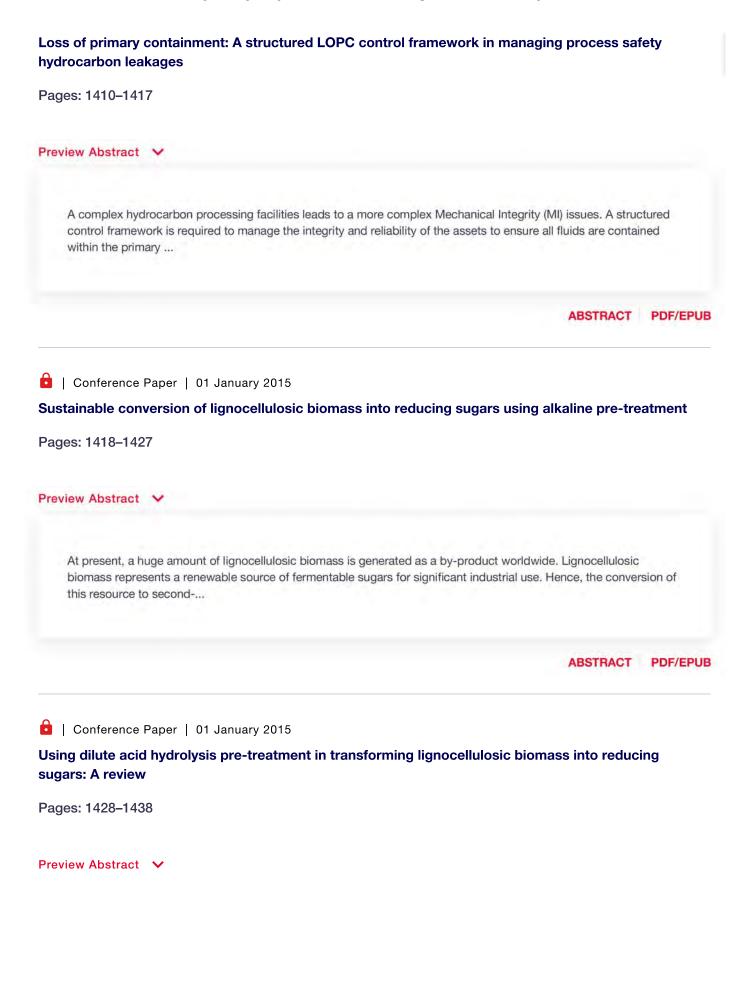


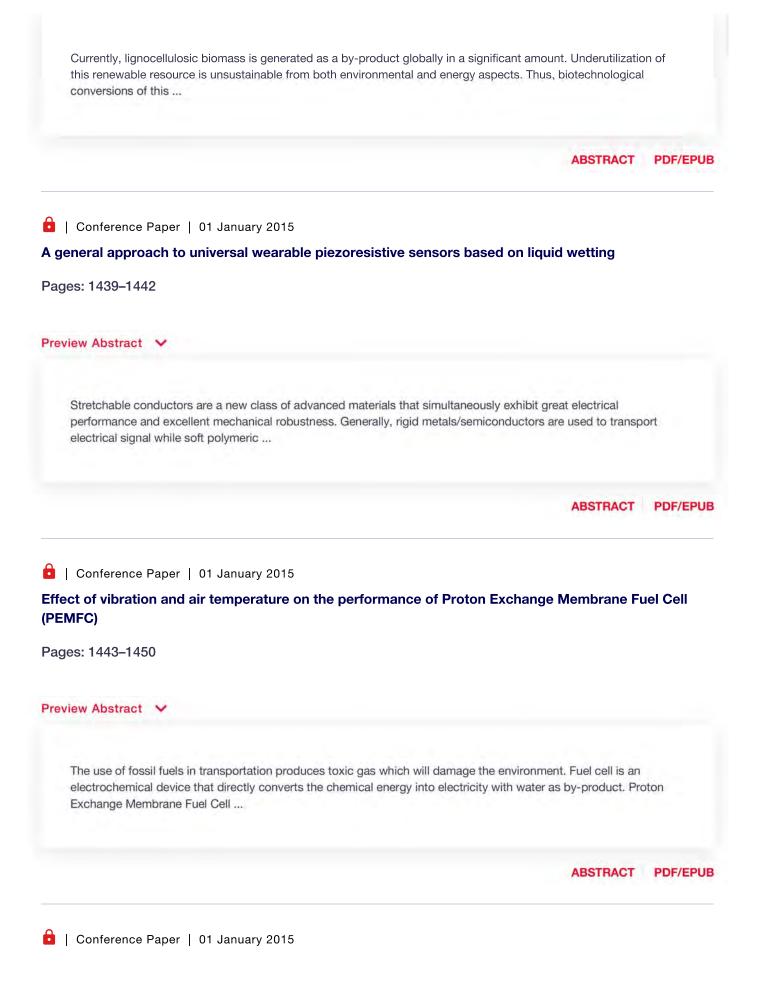


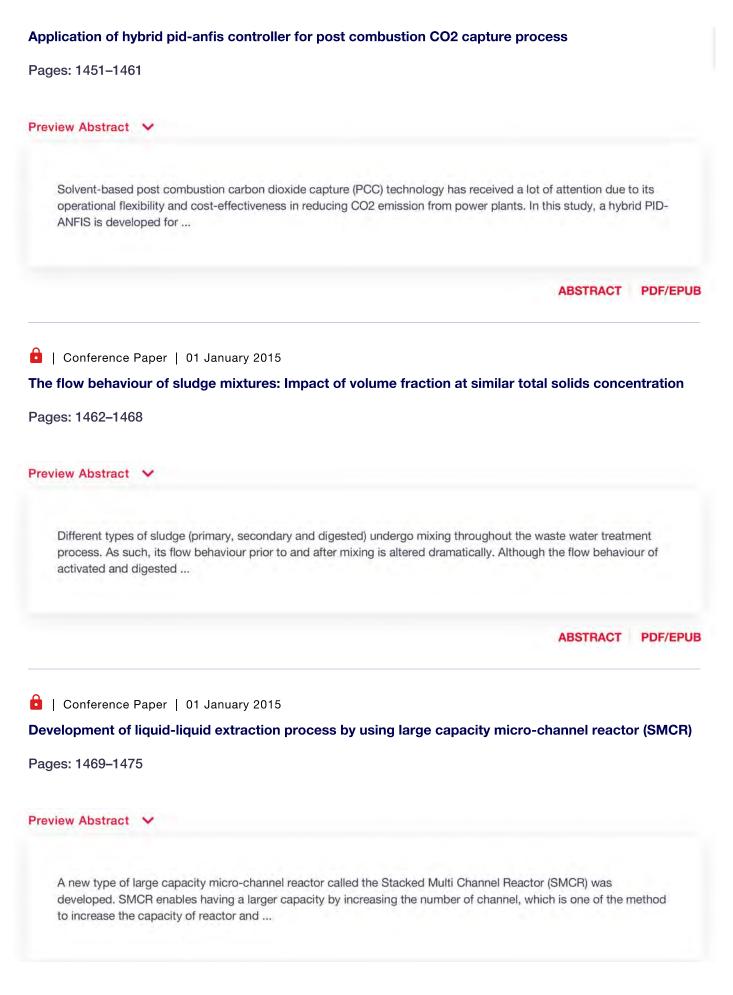


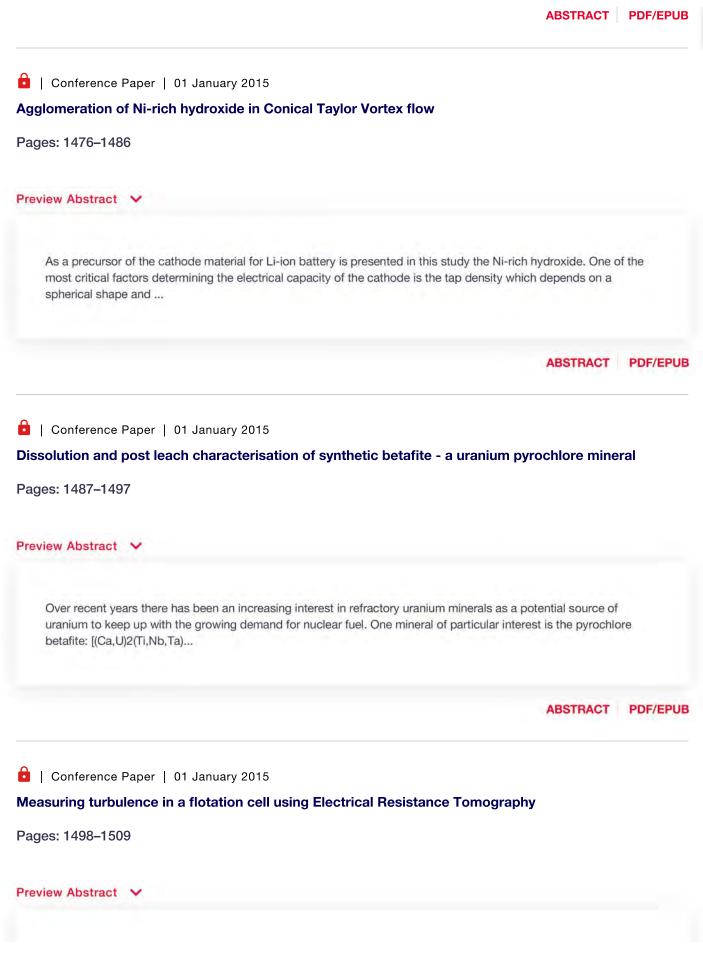


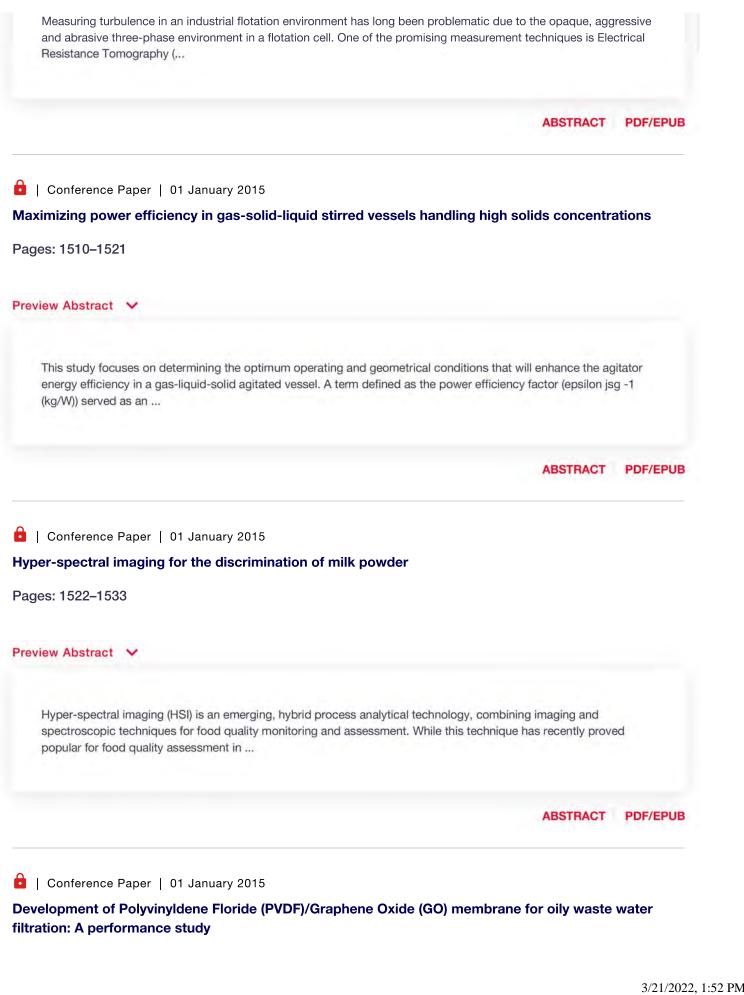


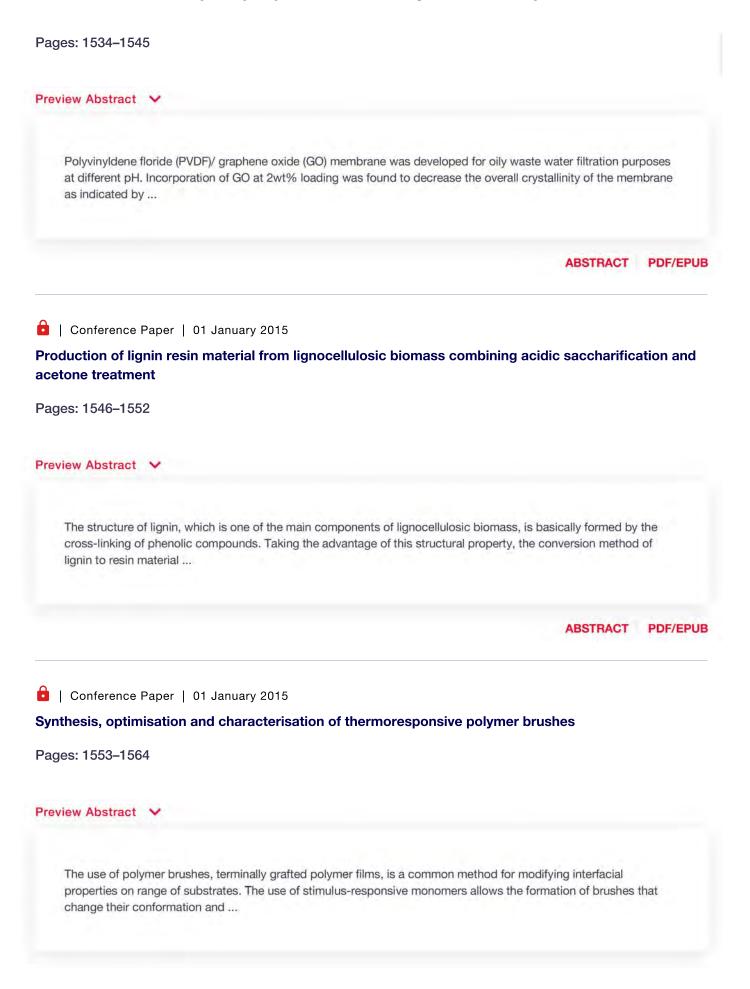


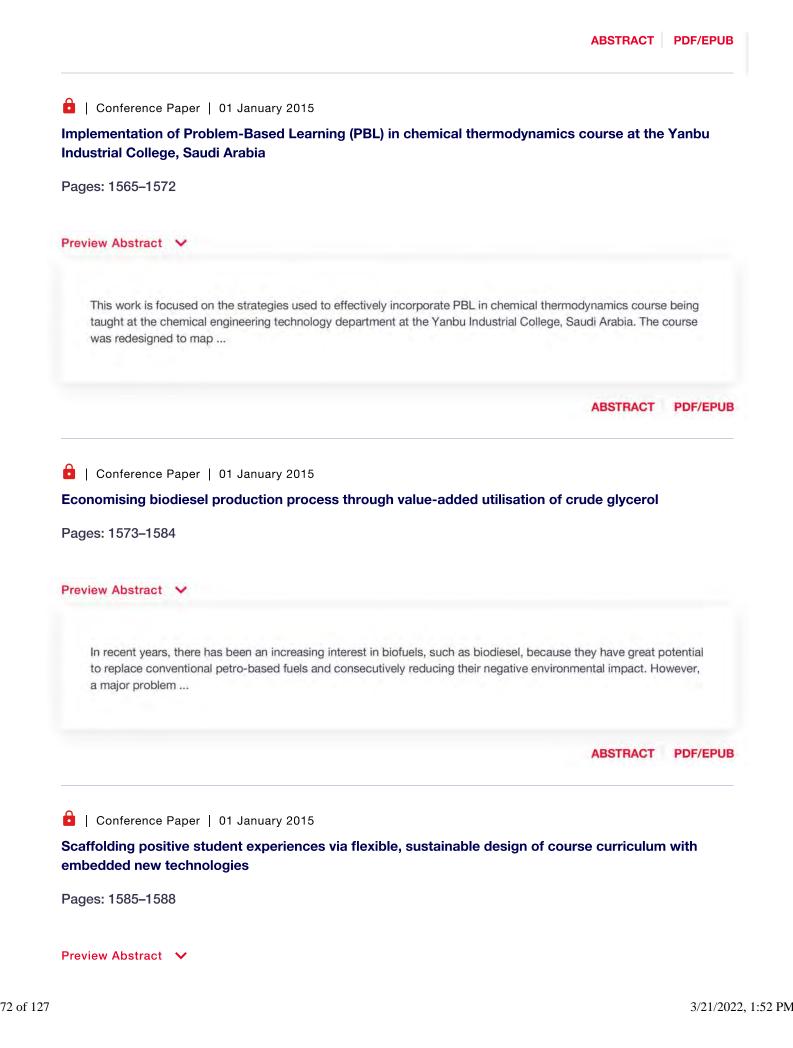


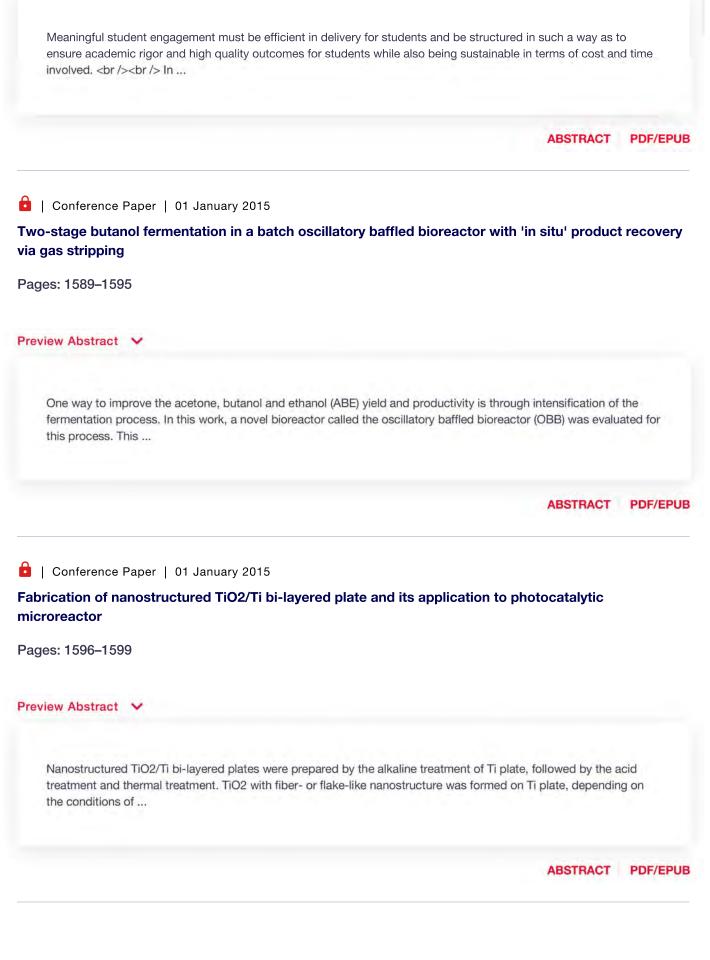


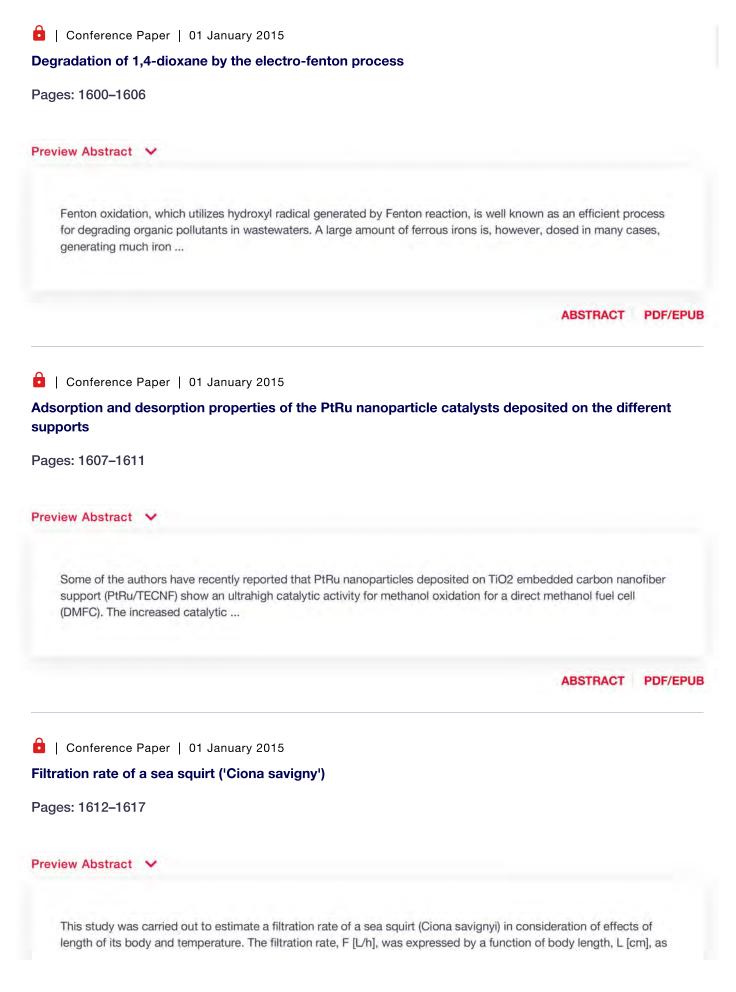


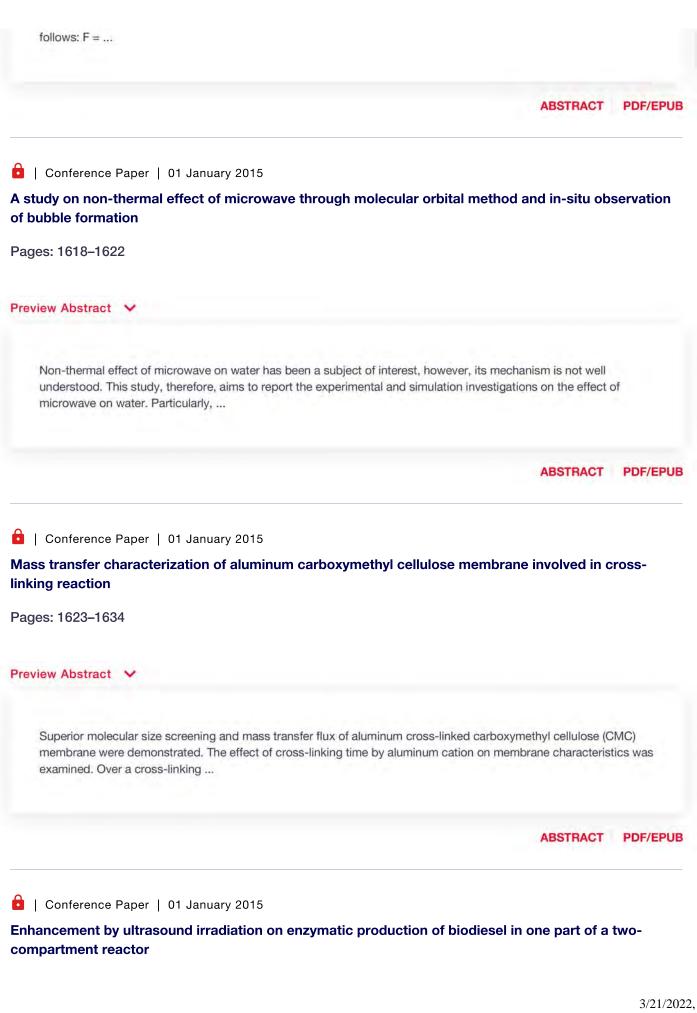


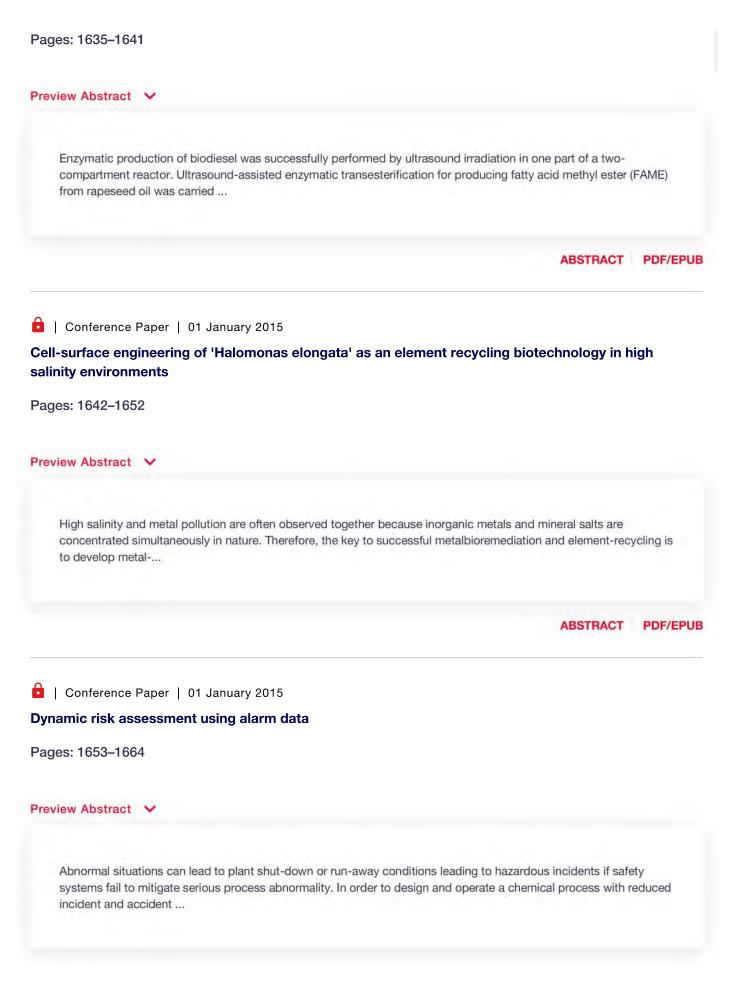


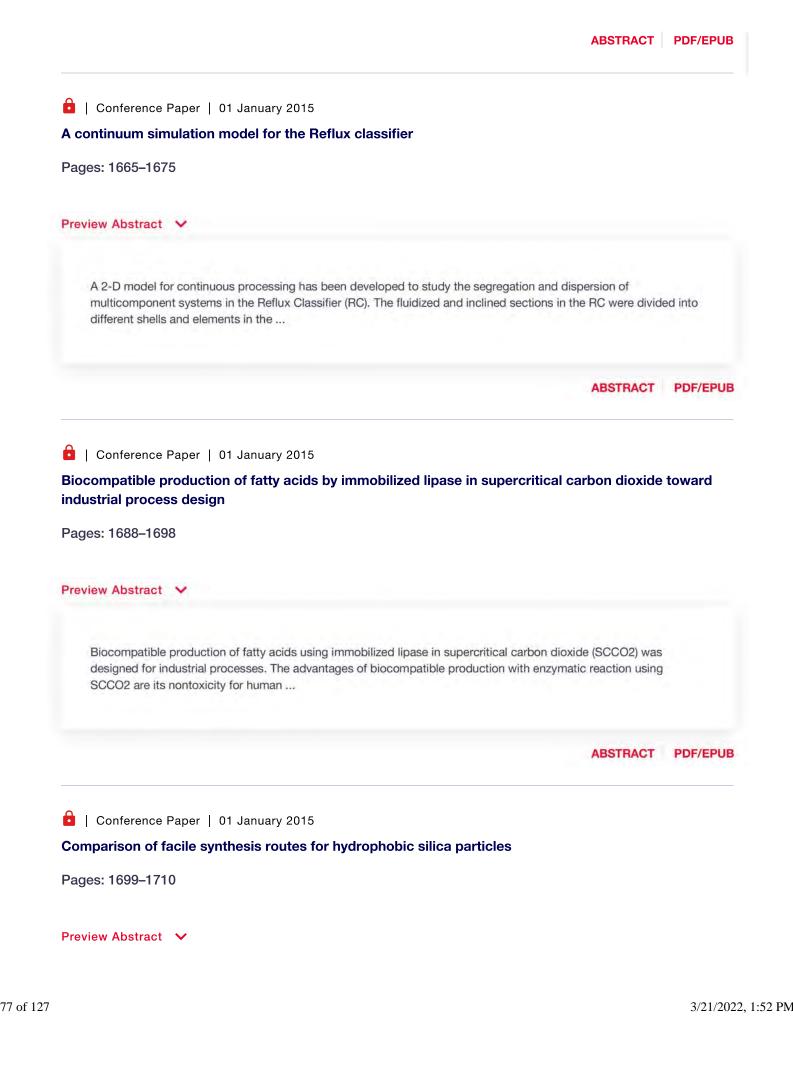


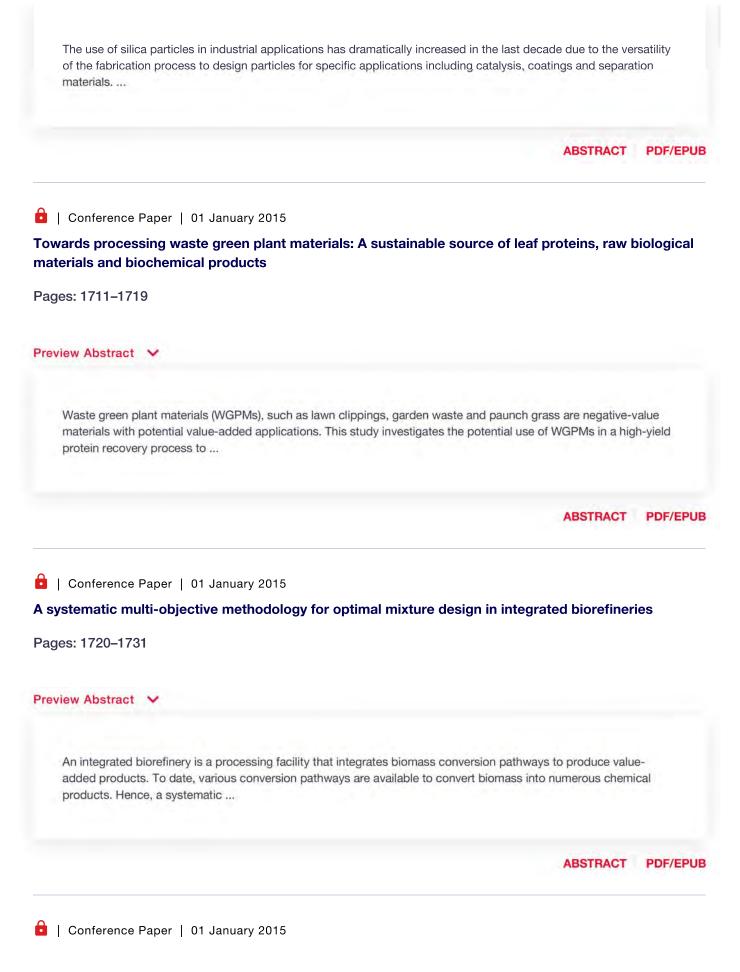


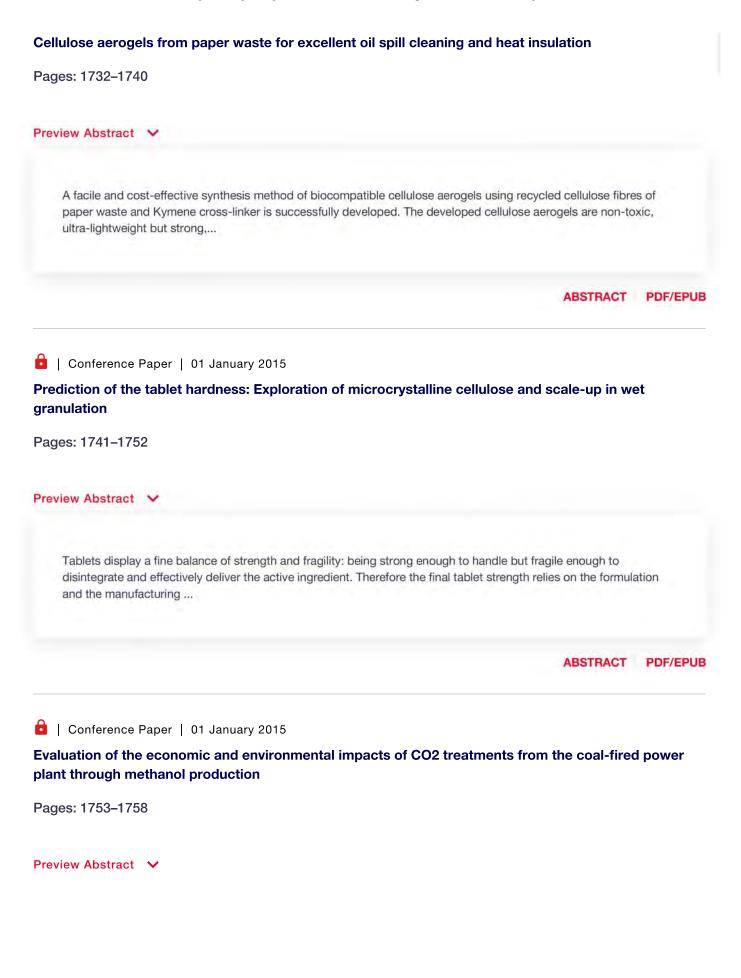


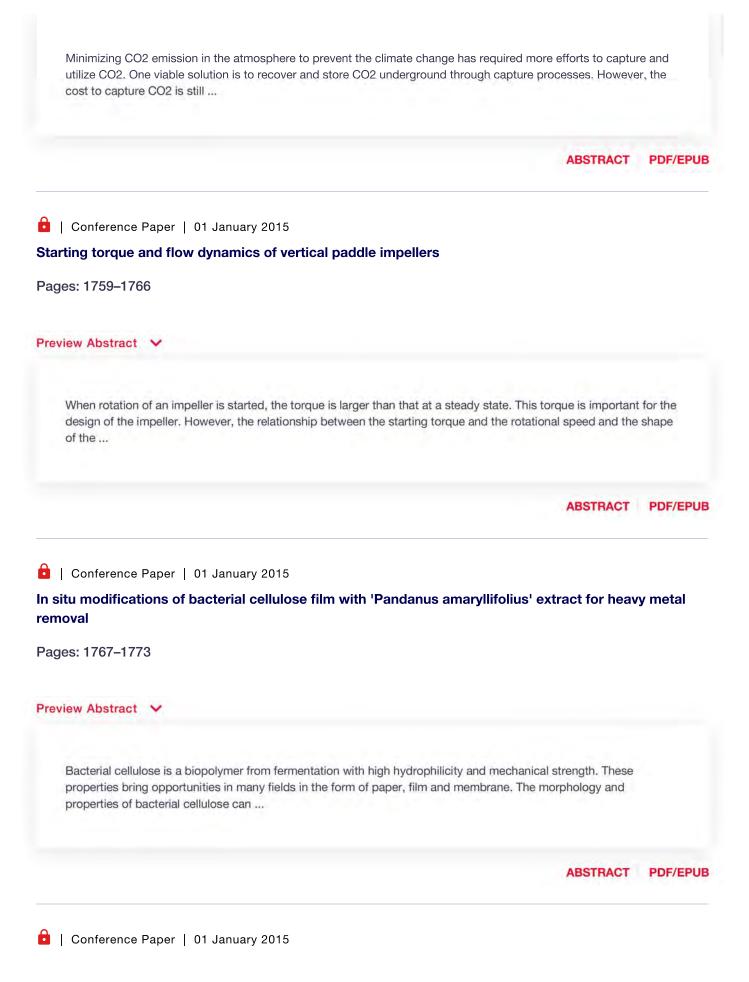




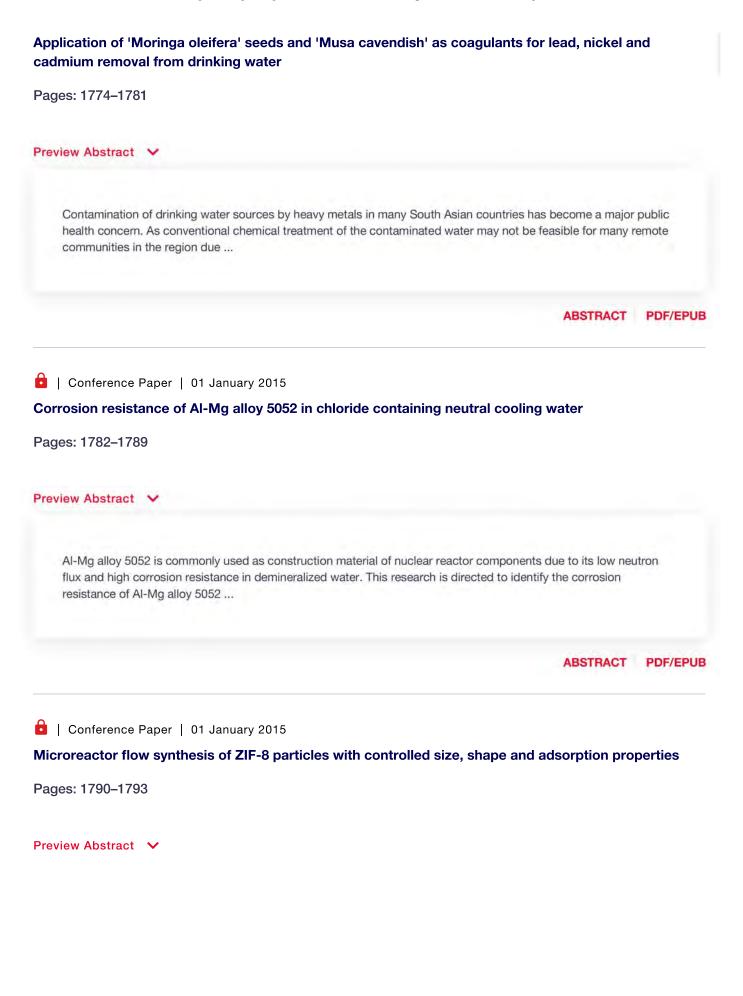


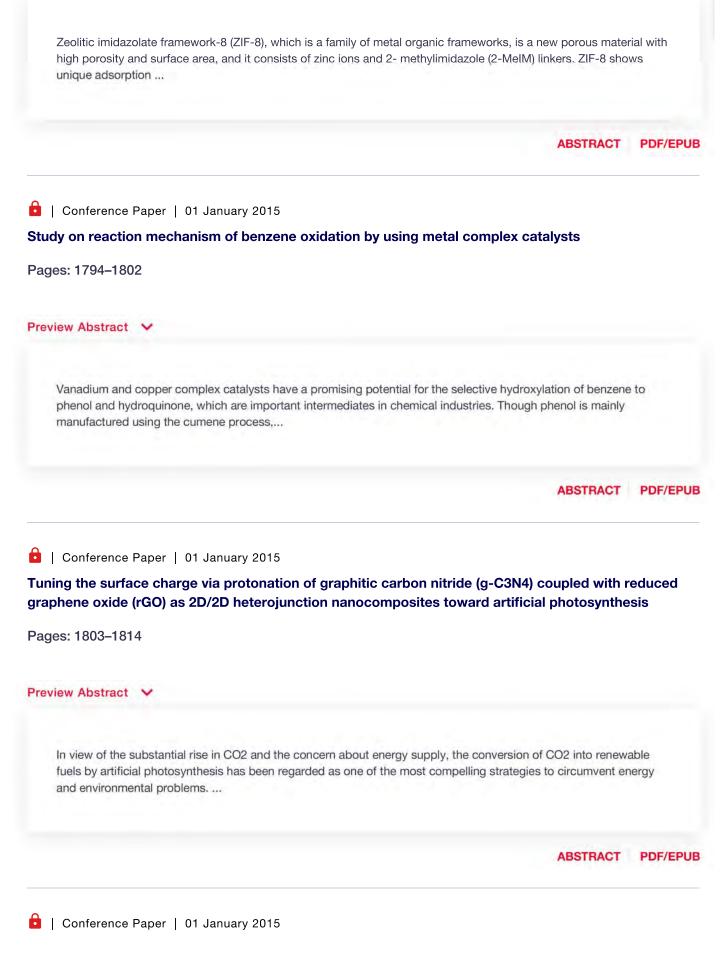


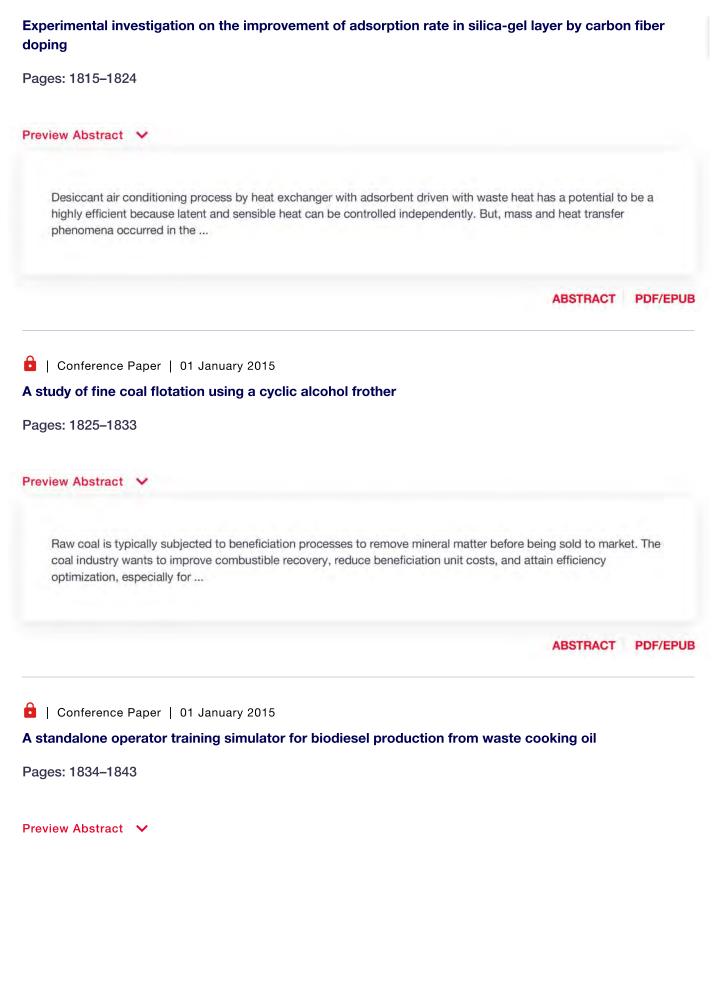




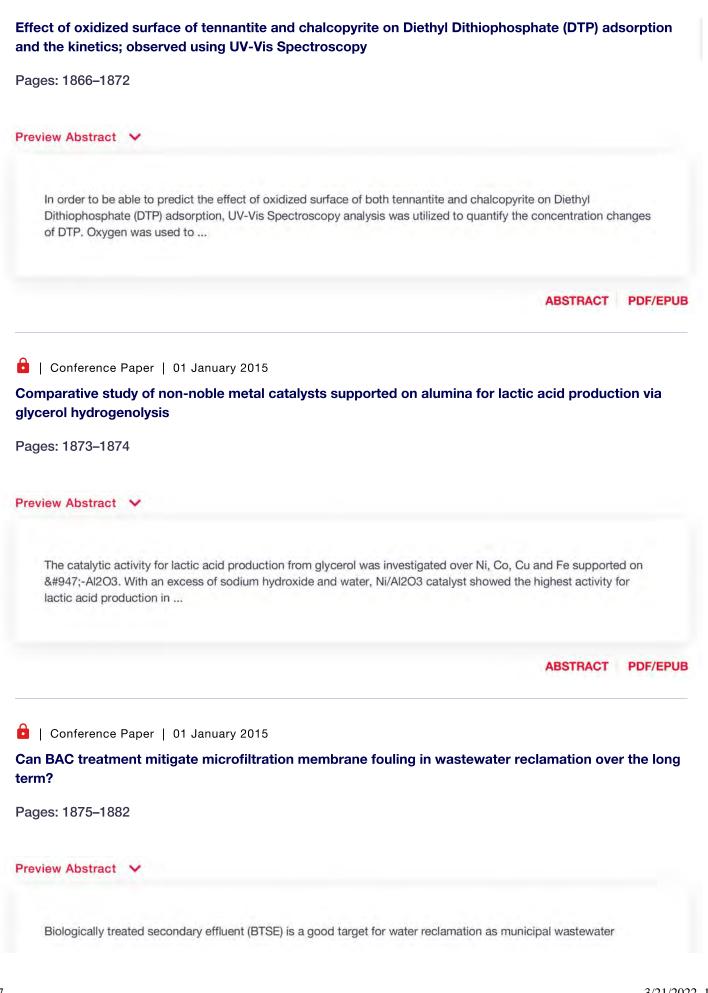
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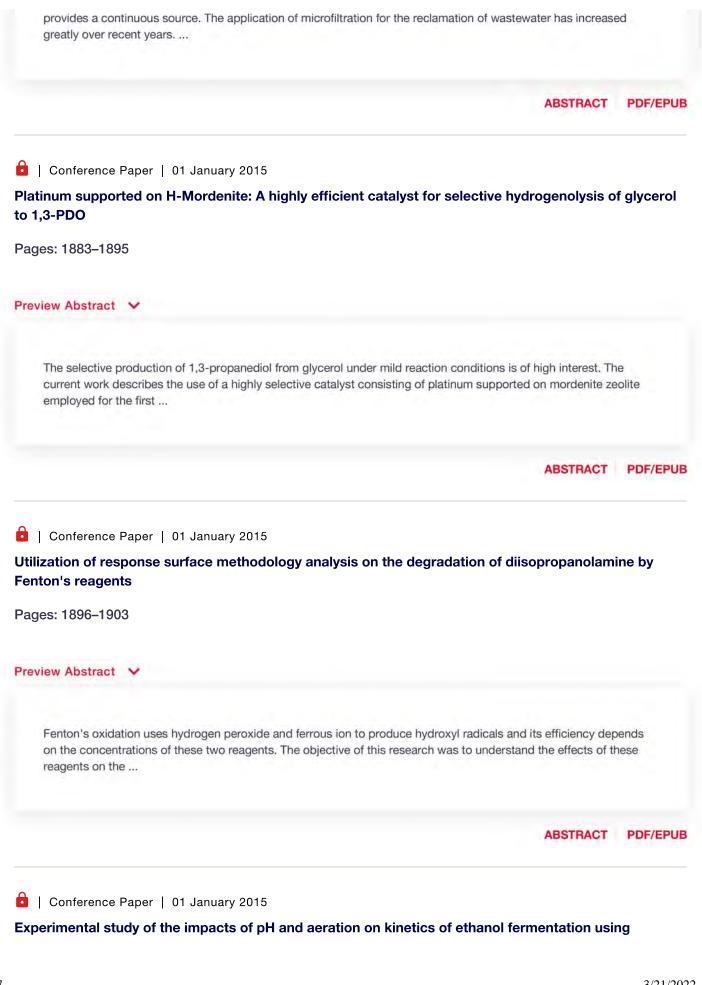






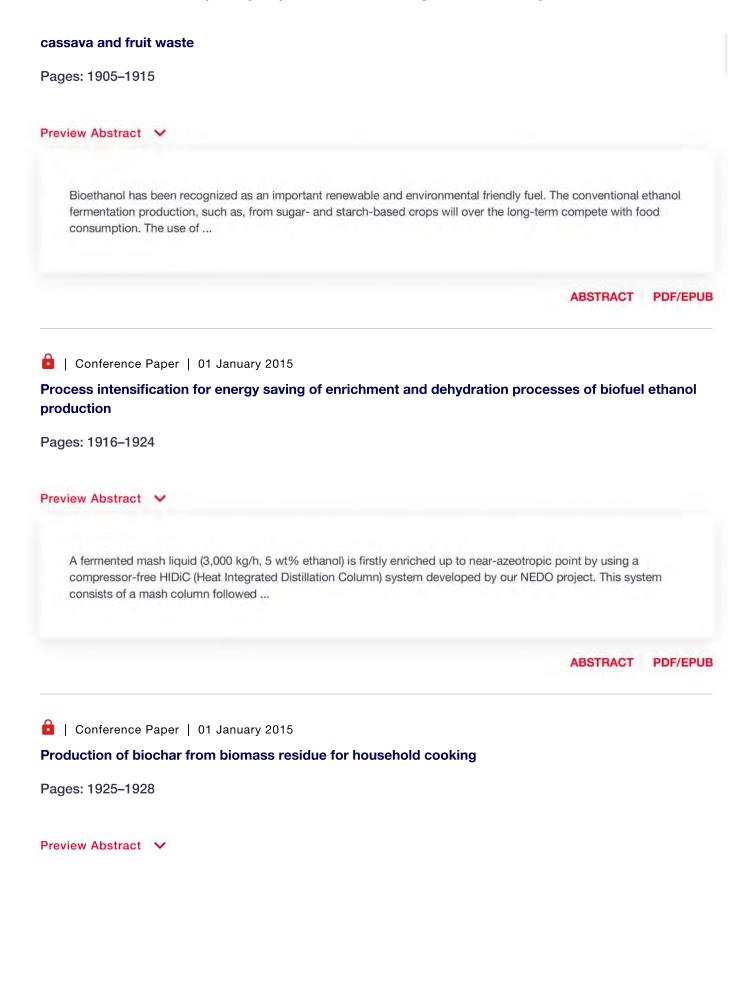
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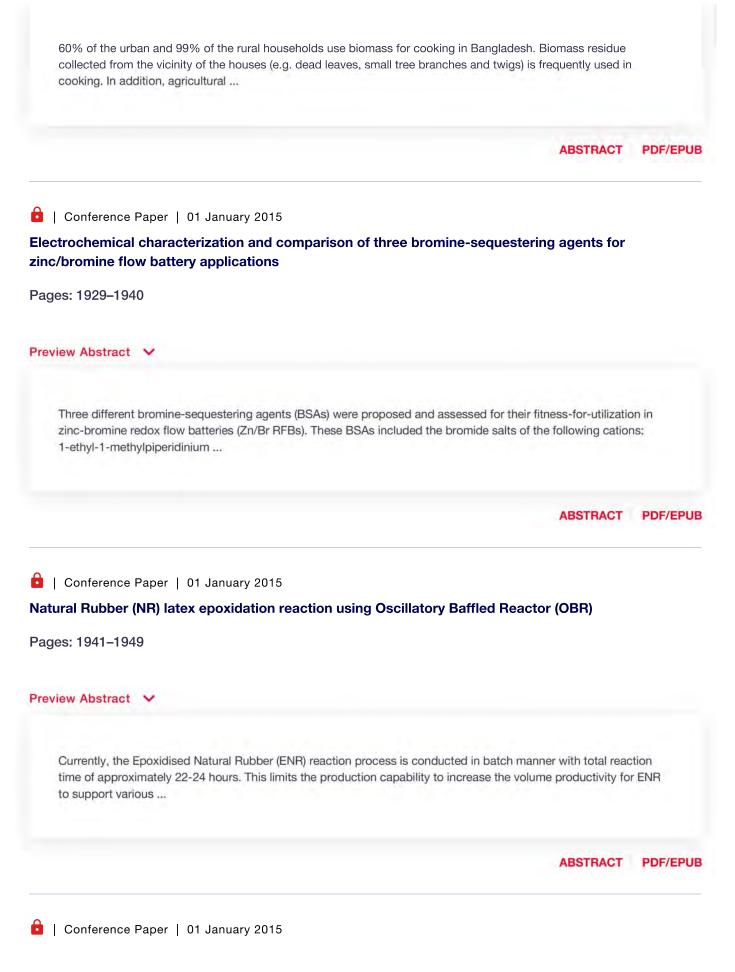


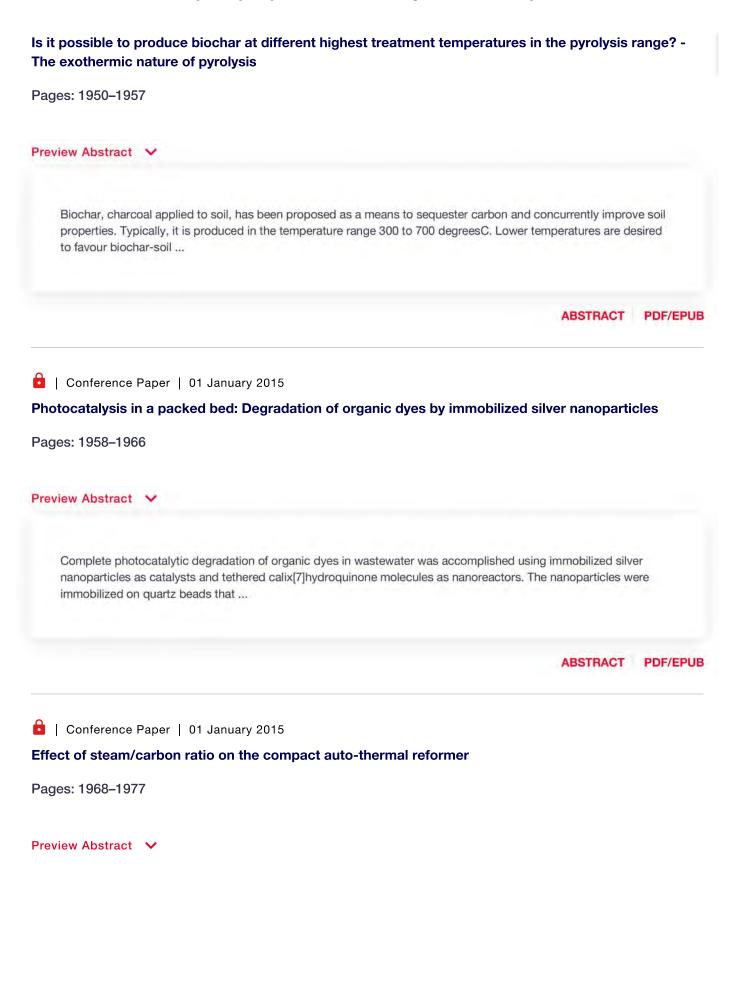


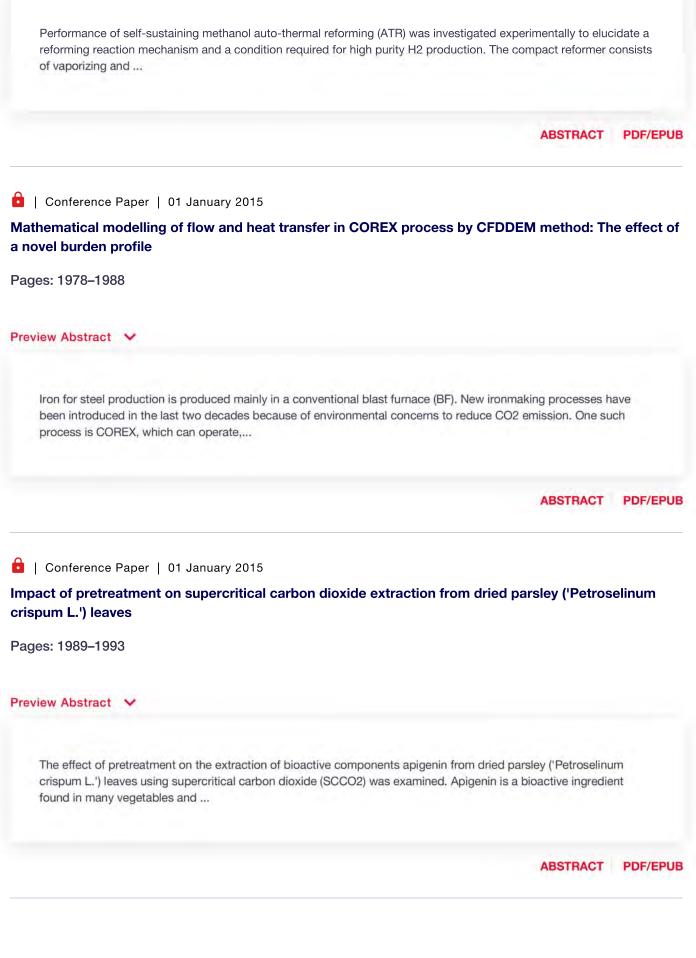
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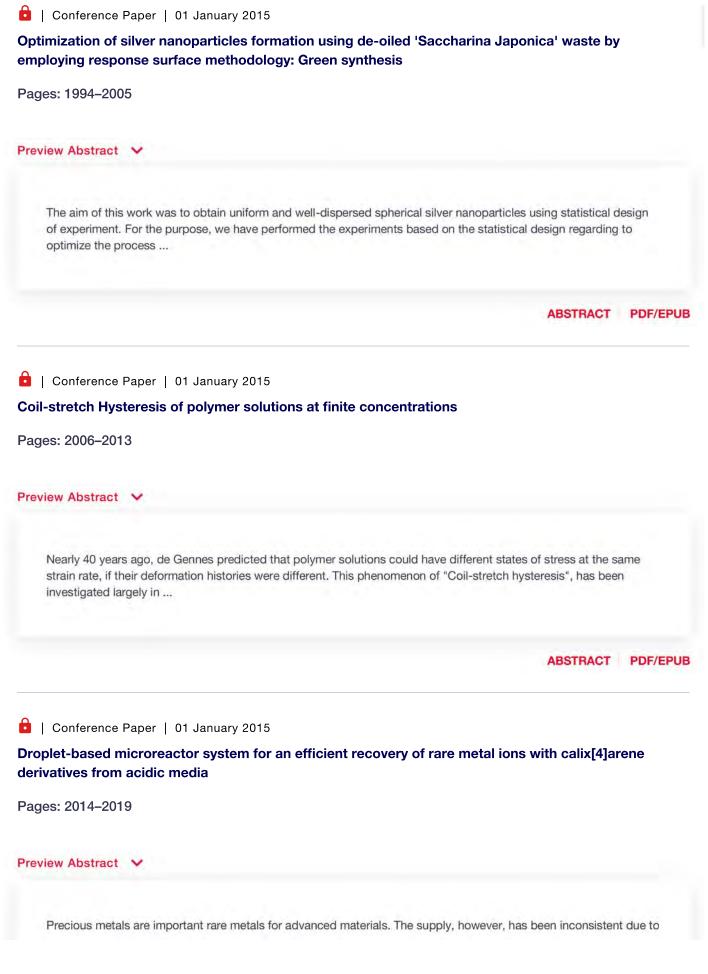
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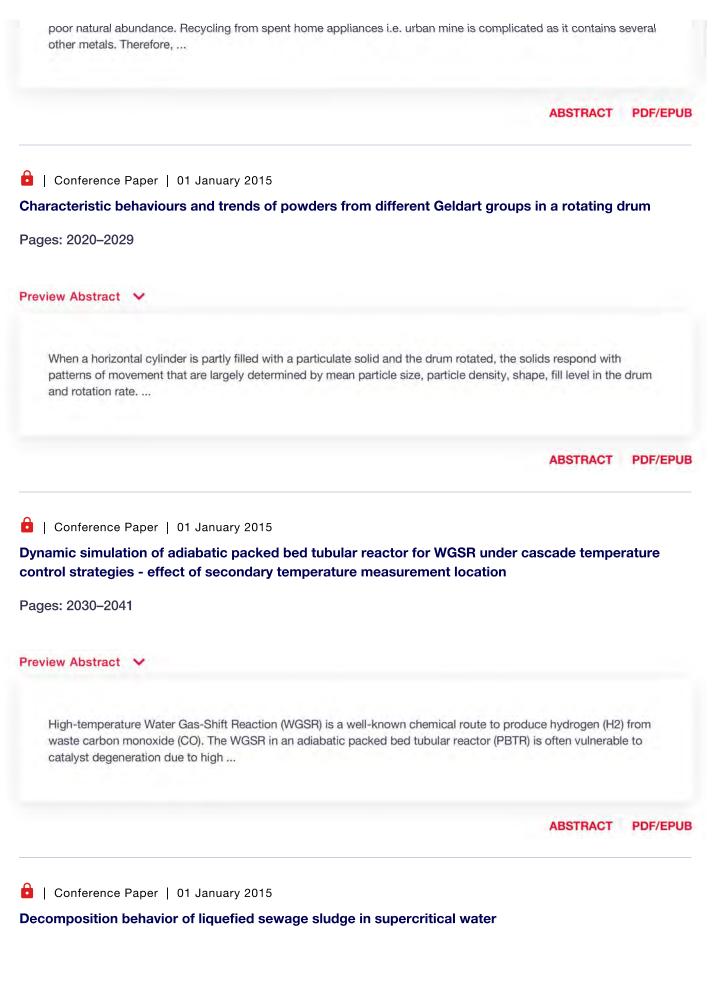


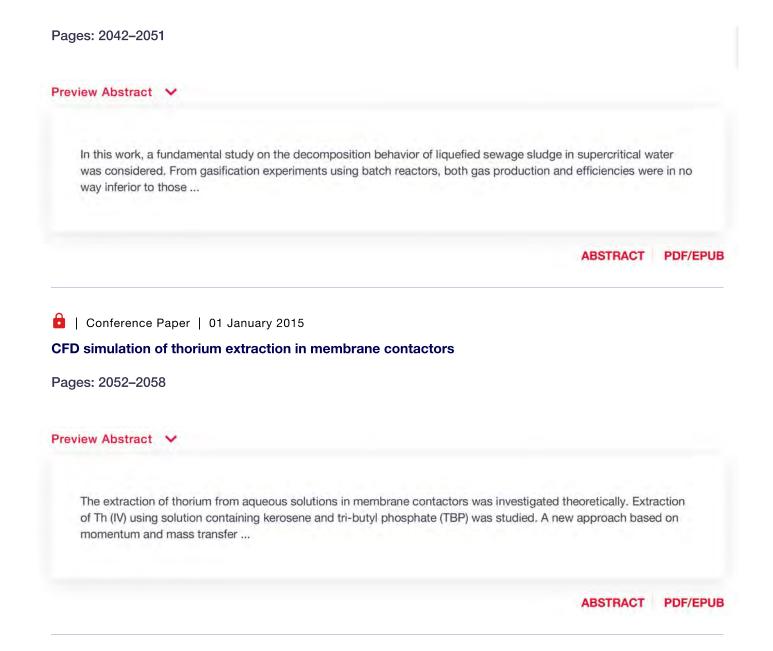


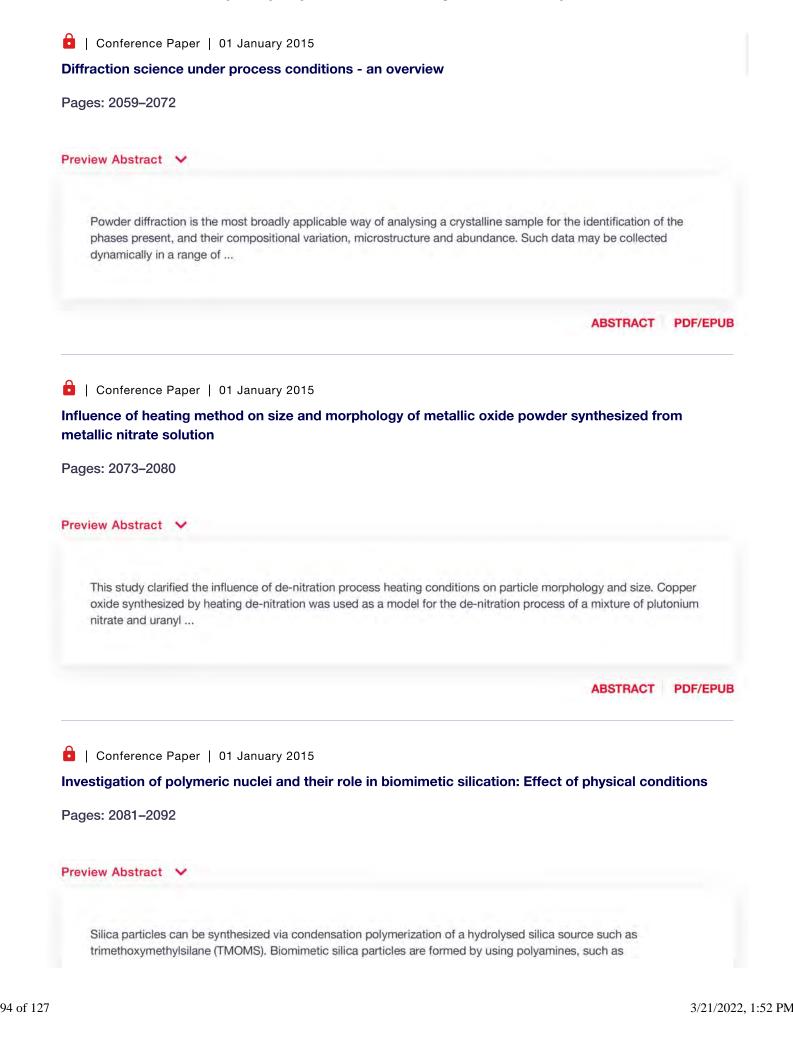


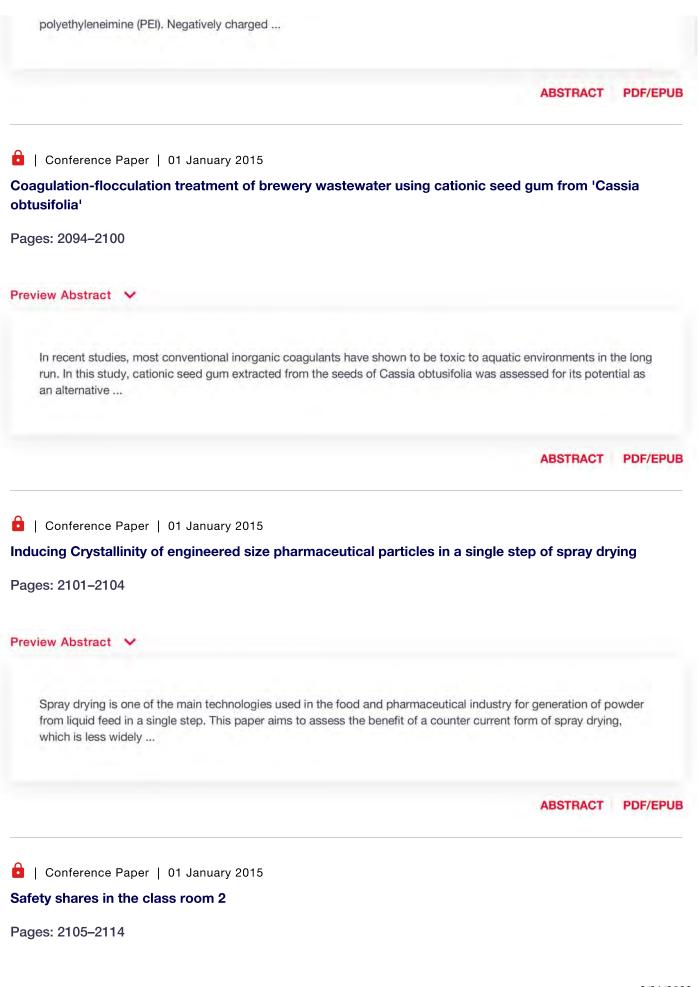


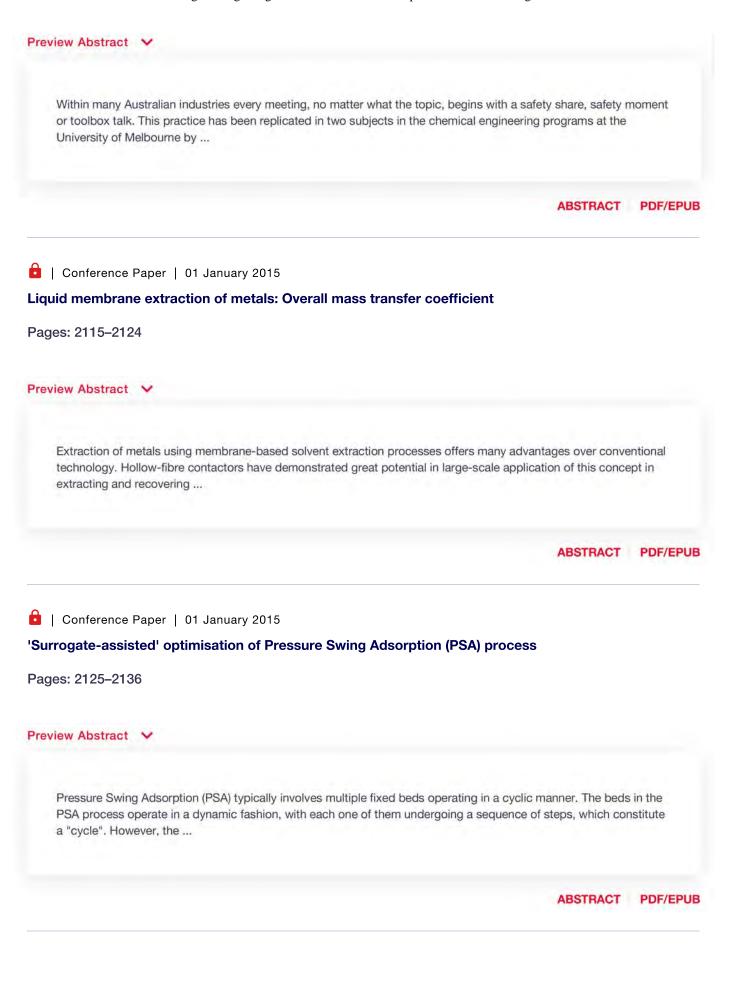














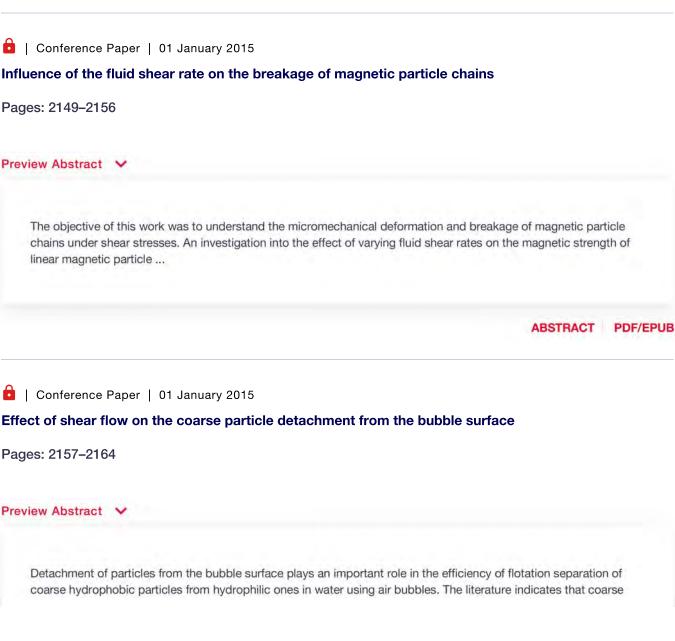
Comparative evaluation of hydroxyl (HO) and sulfate (SO4-) radical based advanced oxidation process for bisphenol a degradation

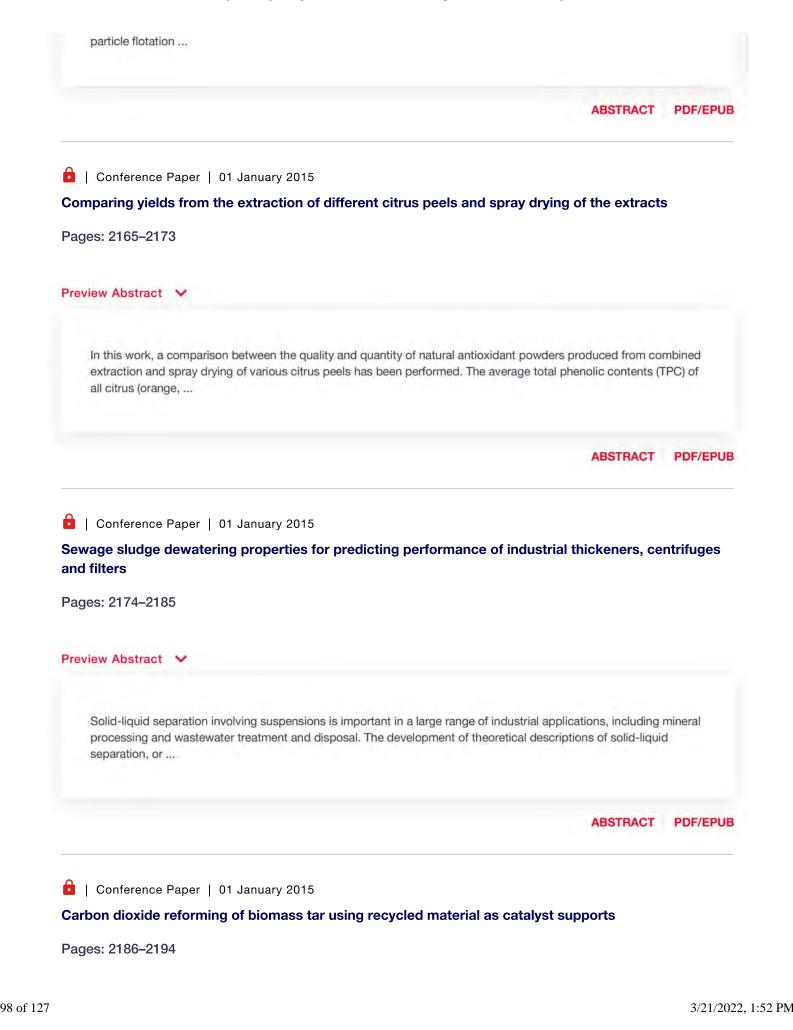
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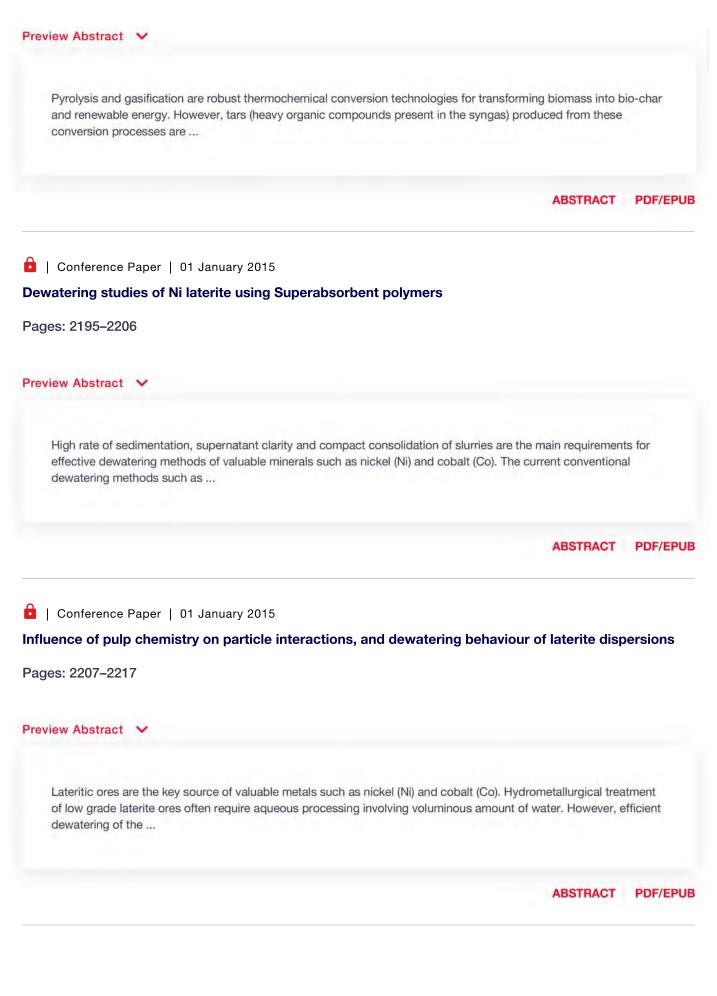
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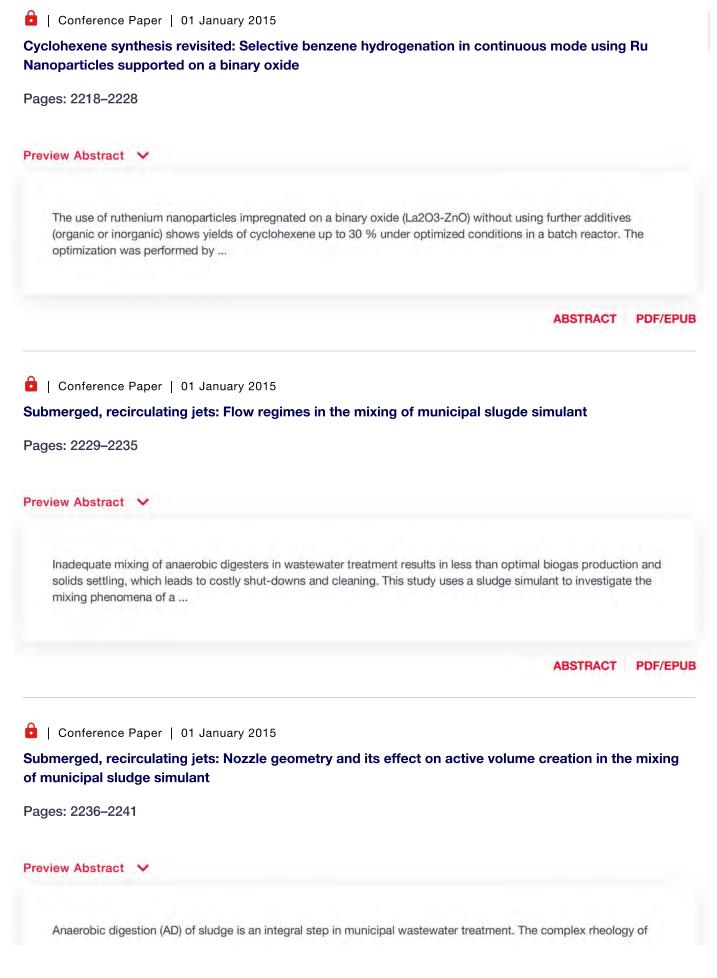
Bisphenol A (BPA) is an industrial chemical and a suspected endocrine disrupting chemical (EDC). It finds its way to water bodies through production units and by leaching from the end products made by BPA-based resins (epoxy and polycarbonate). In the ...

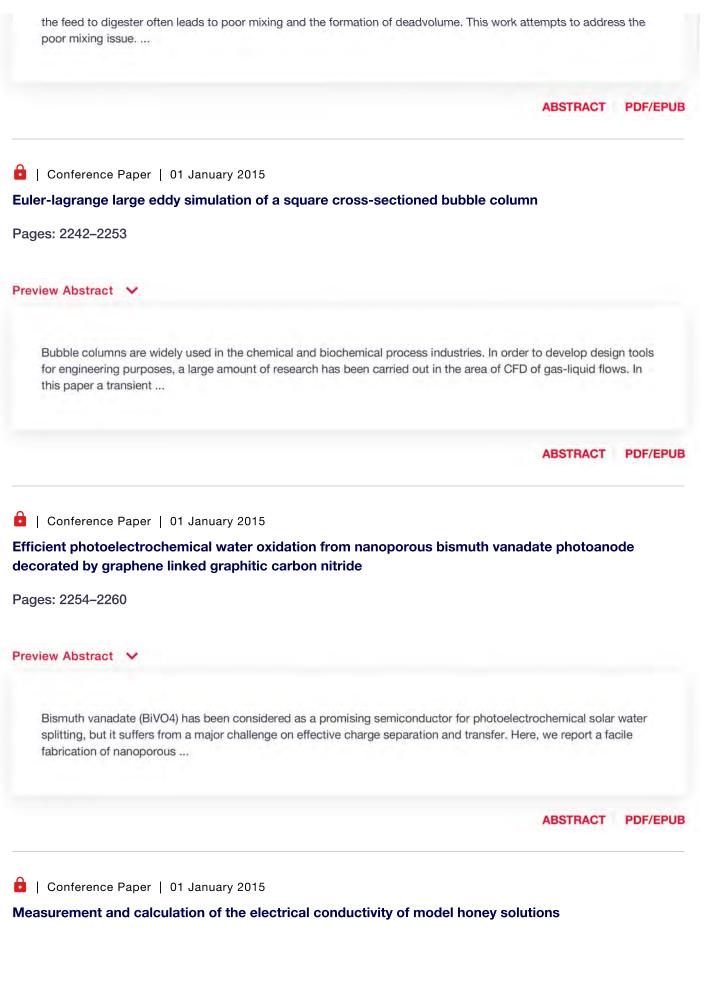
ABSTRACT PDF/EPUB

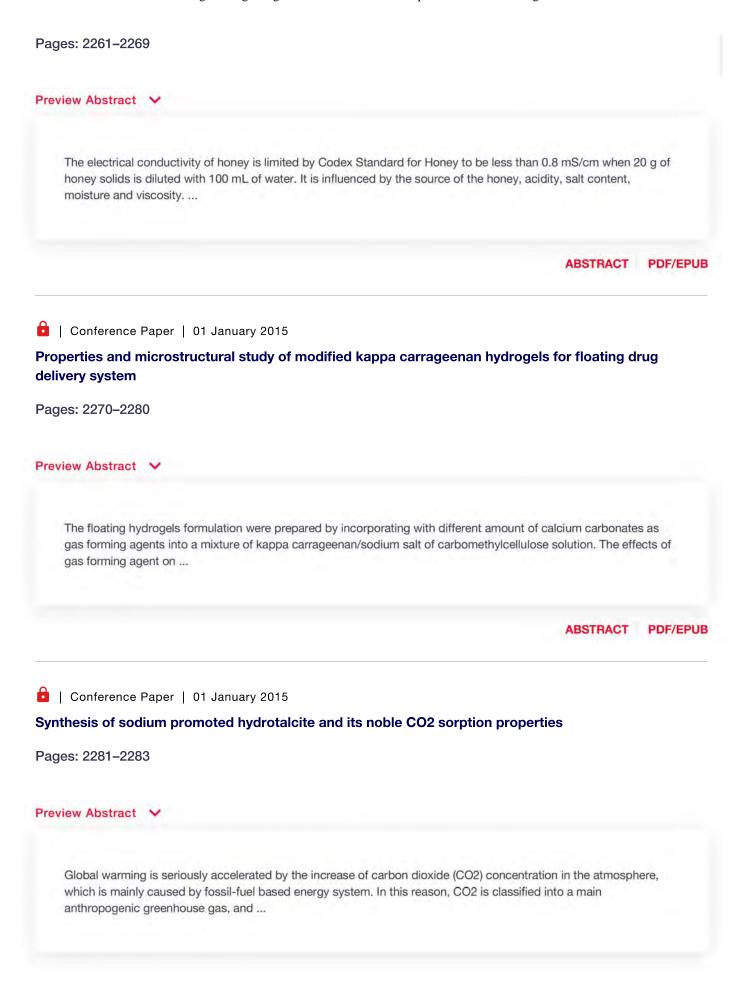


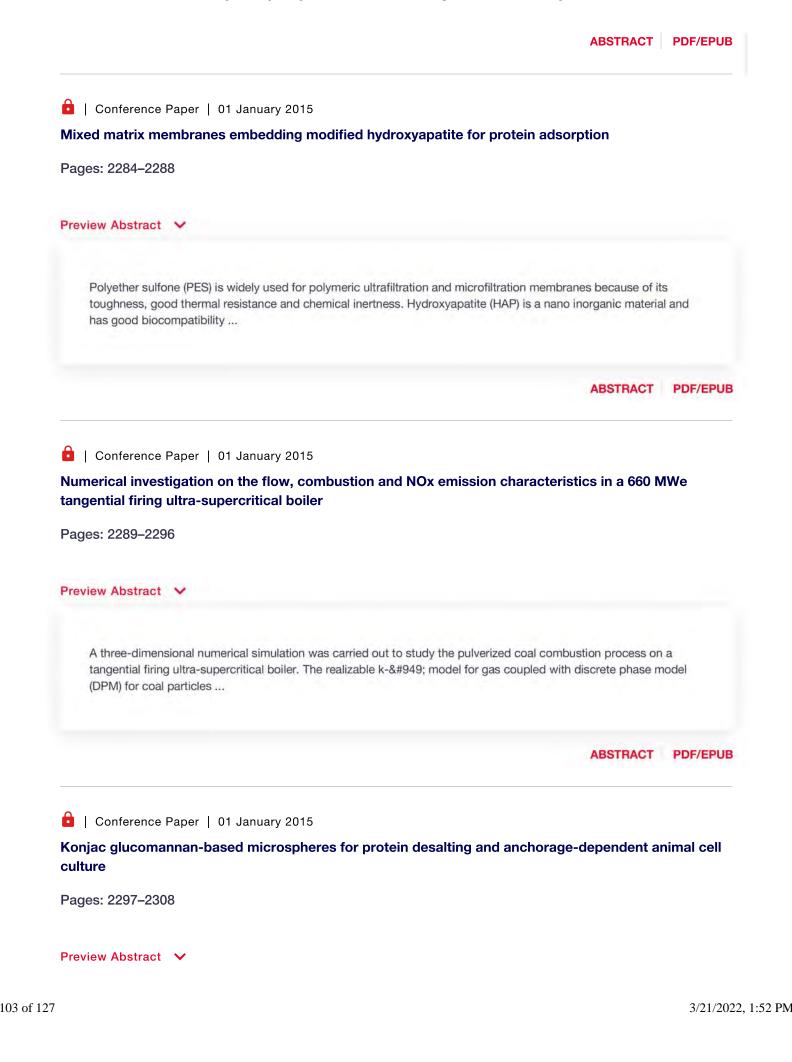


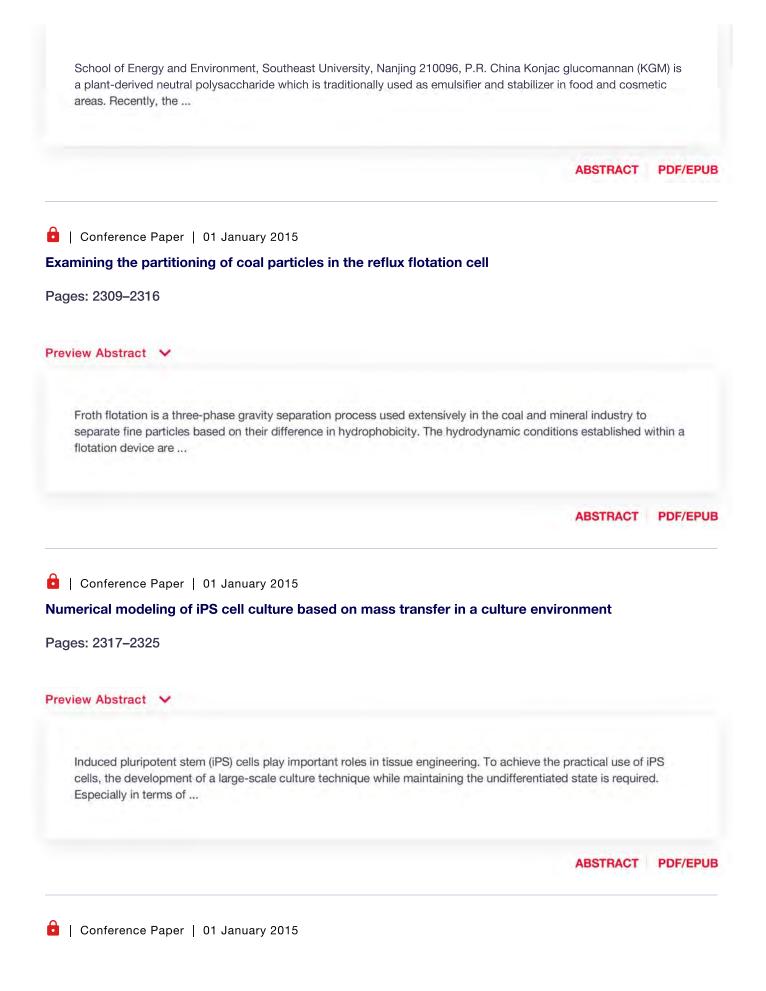


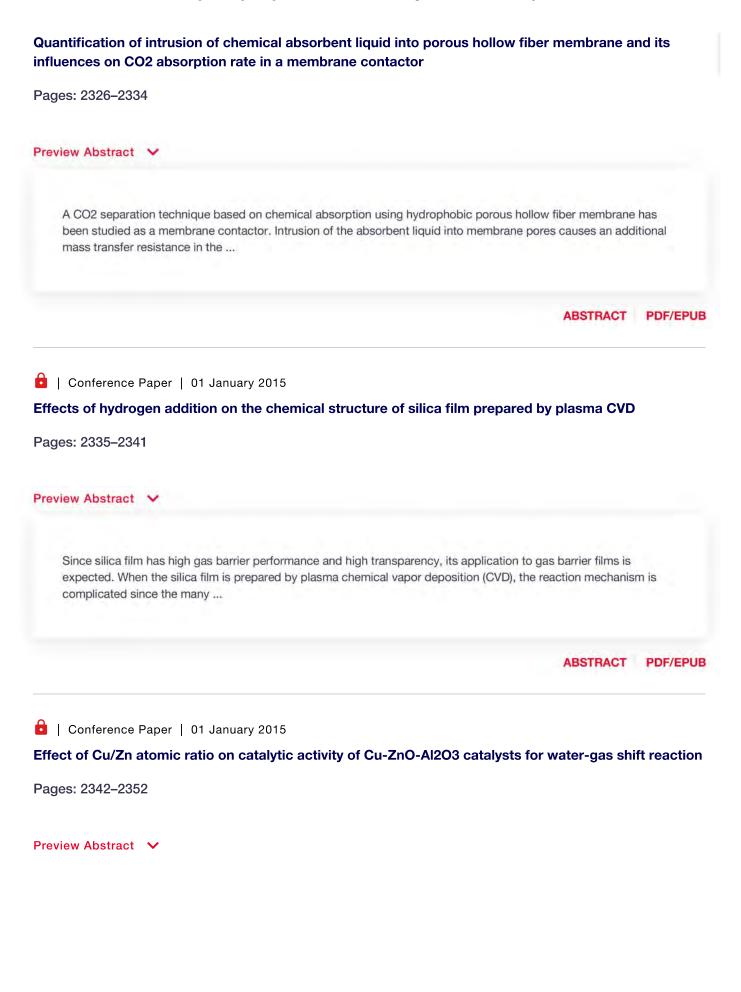


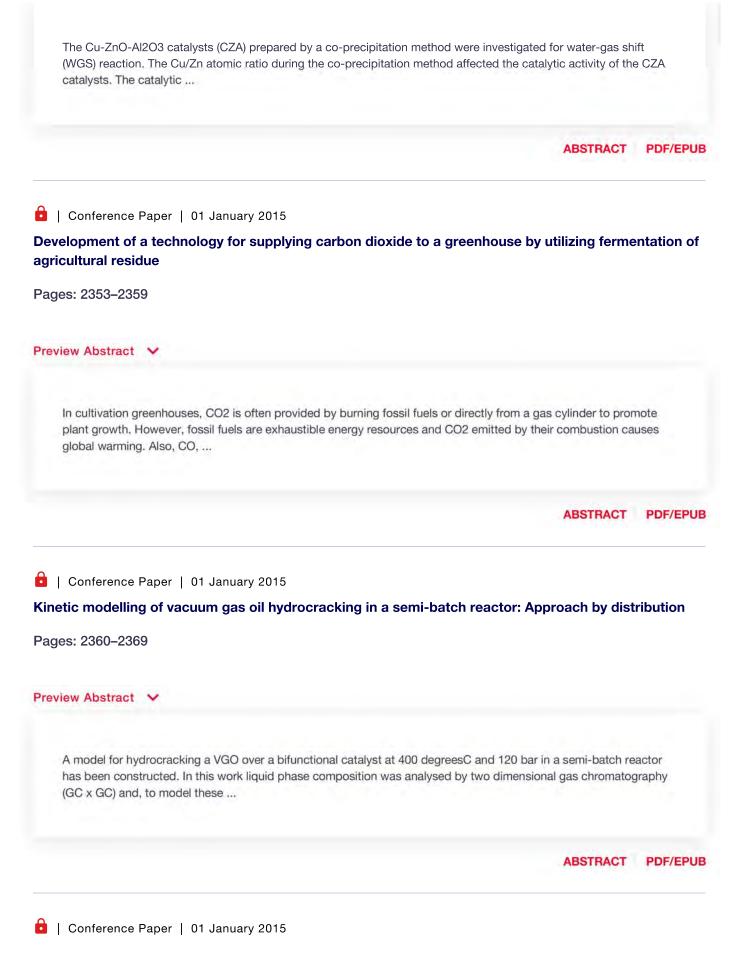


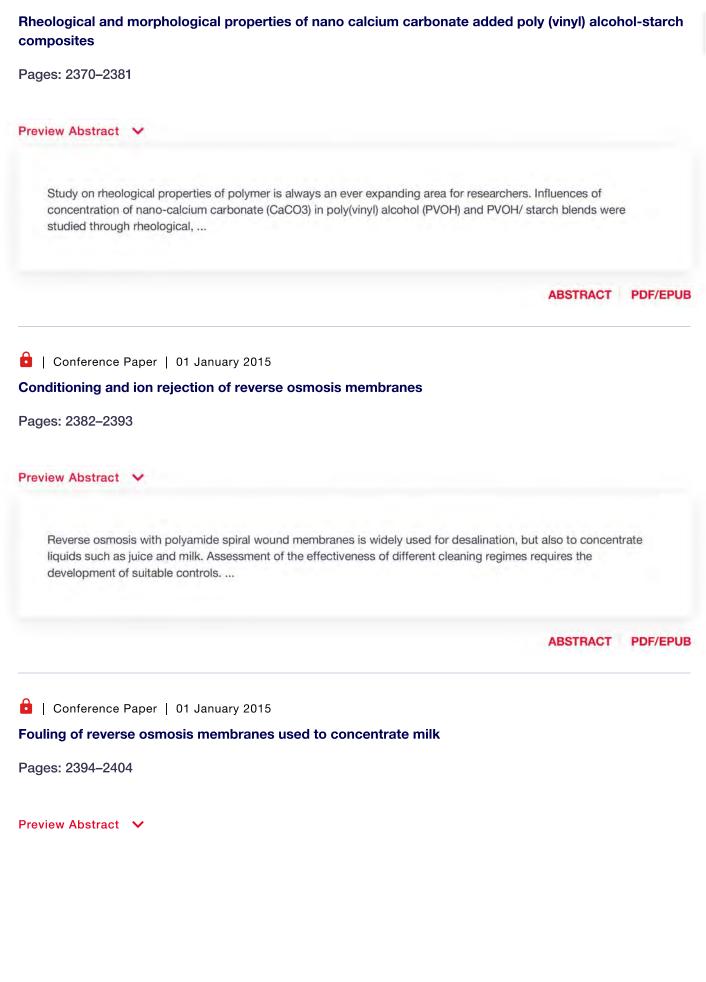


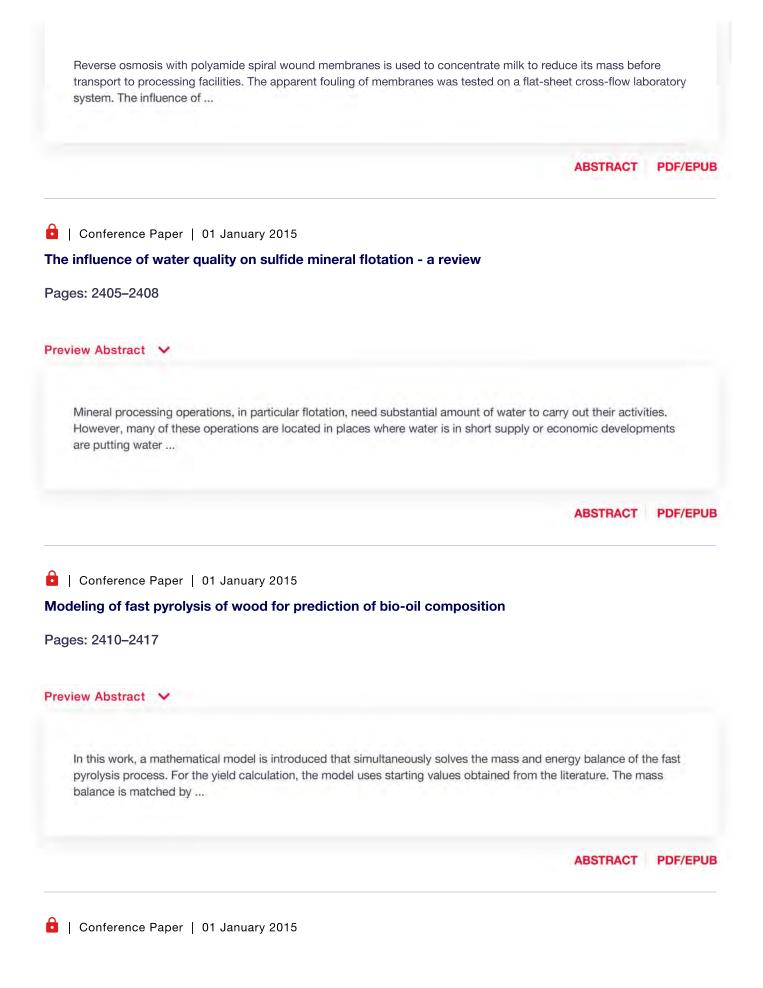


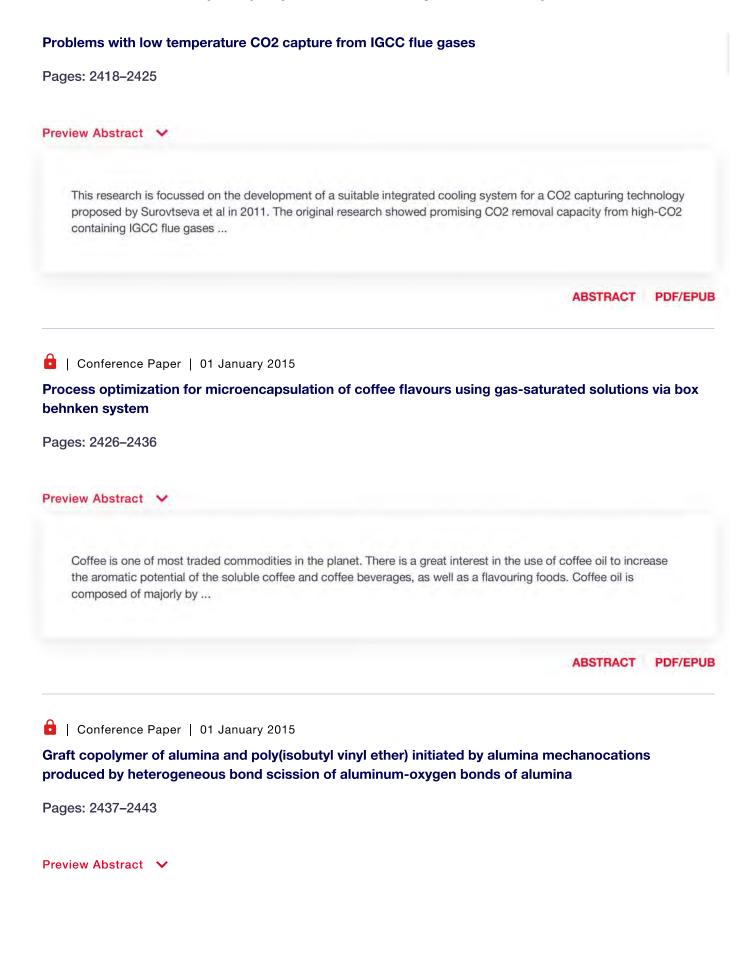


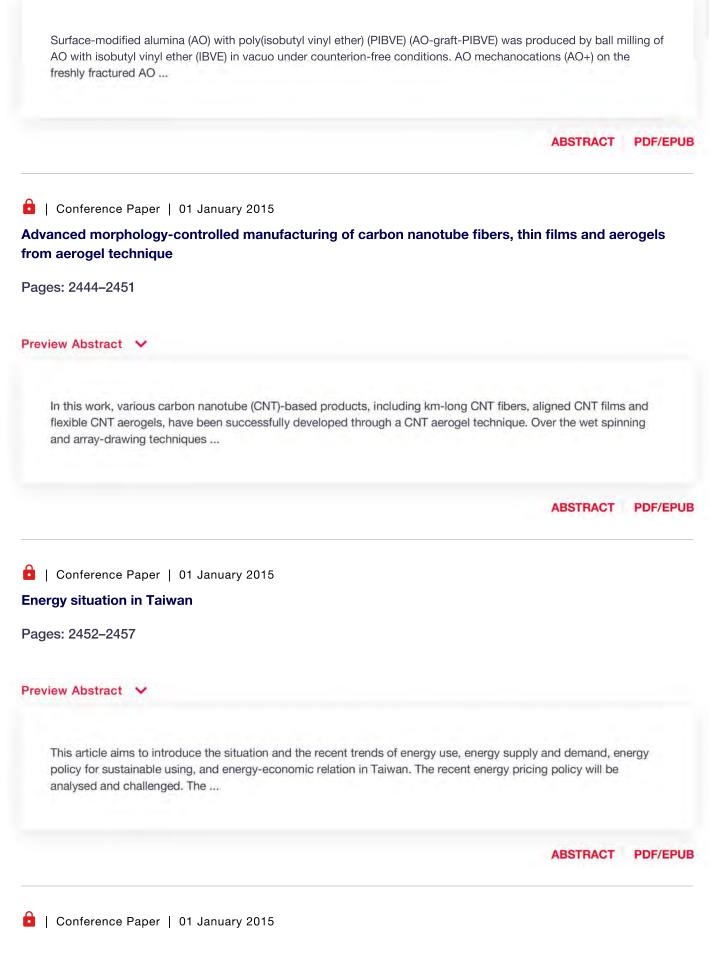


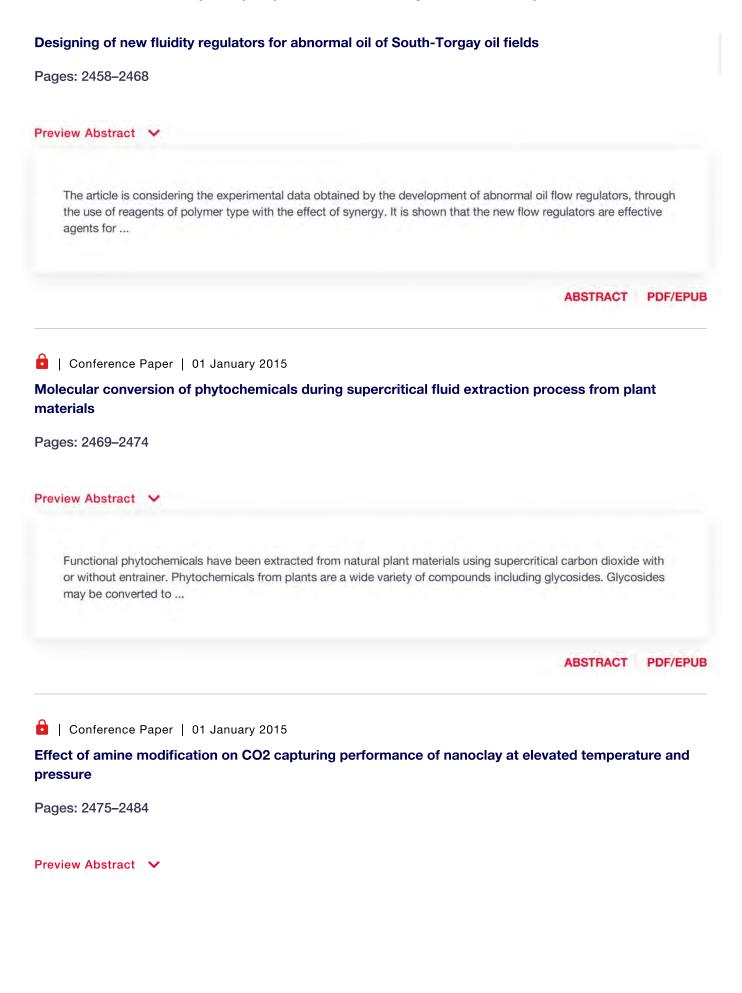


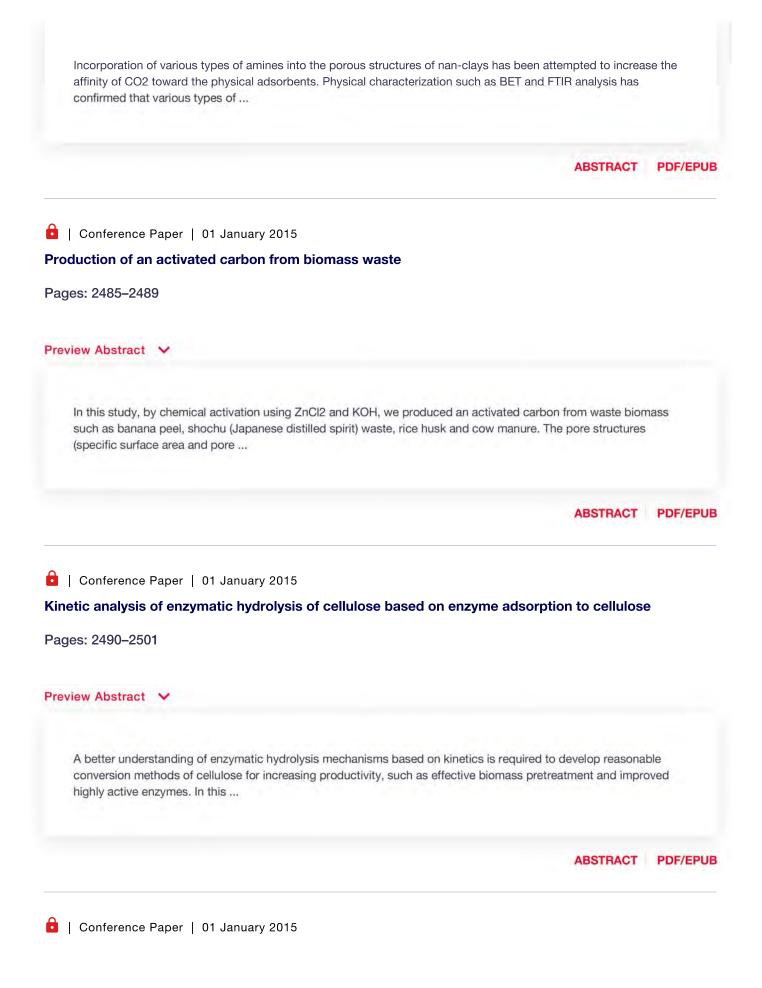


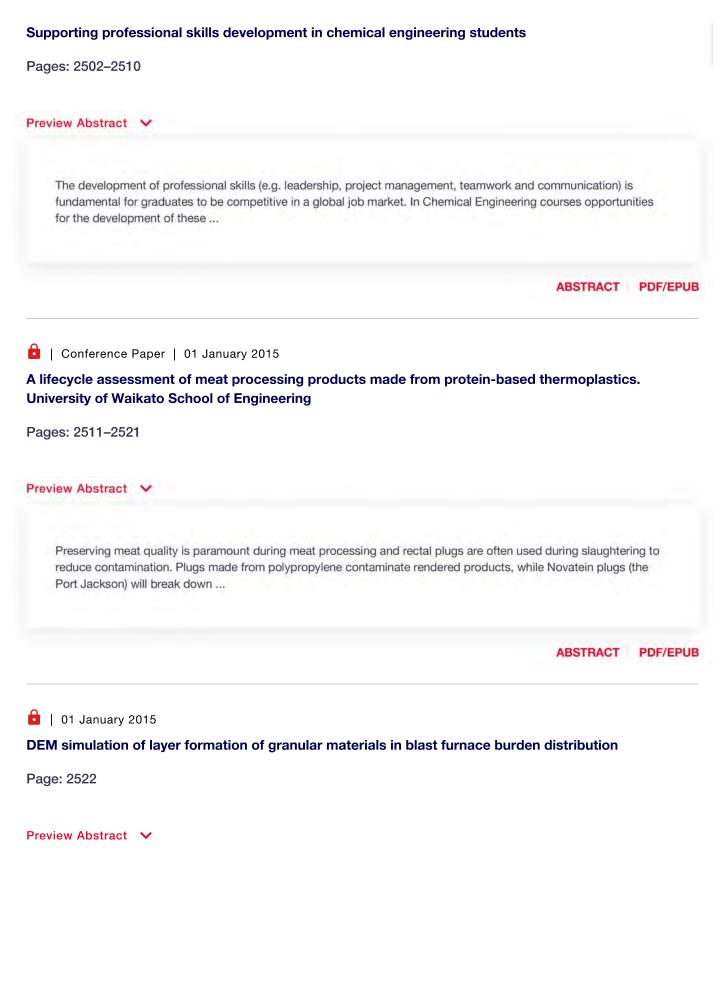


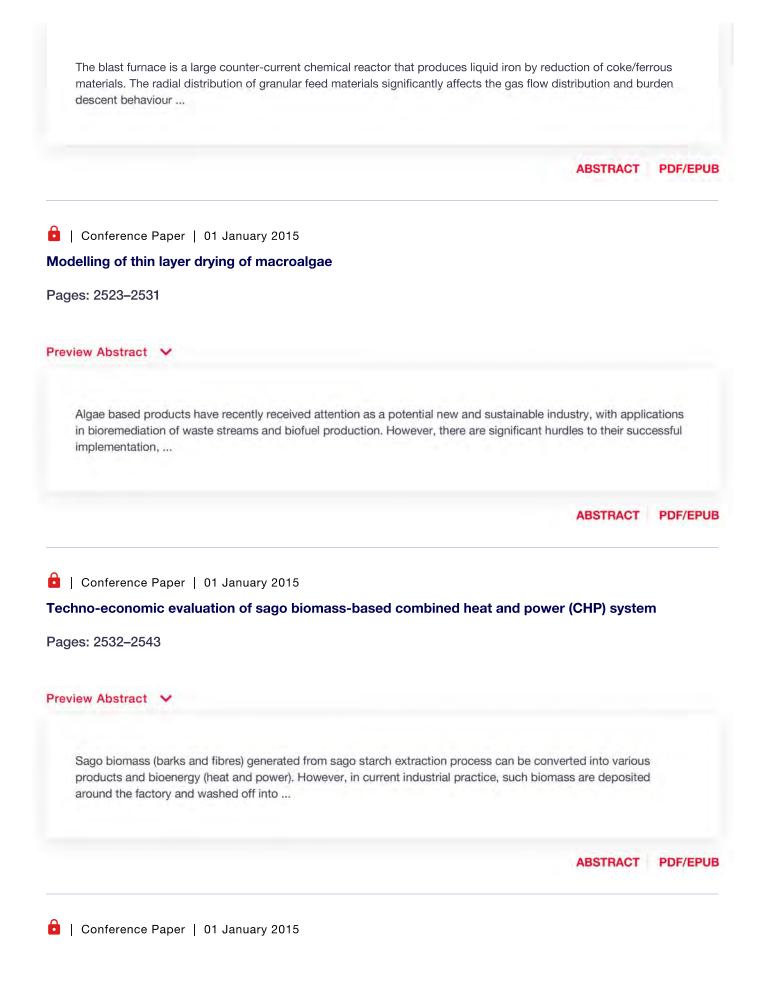


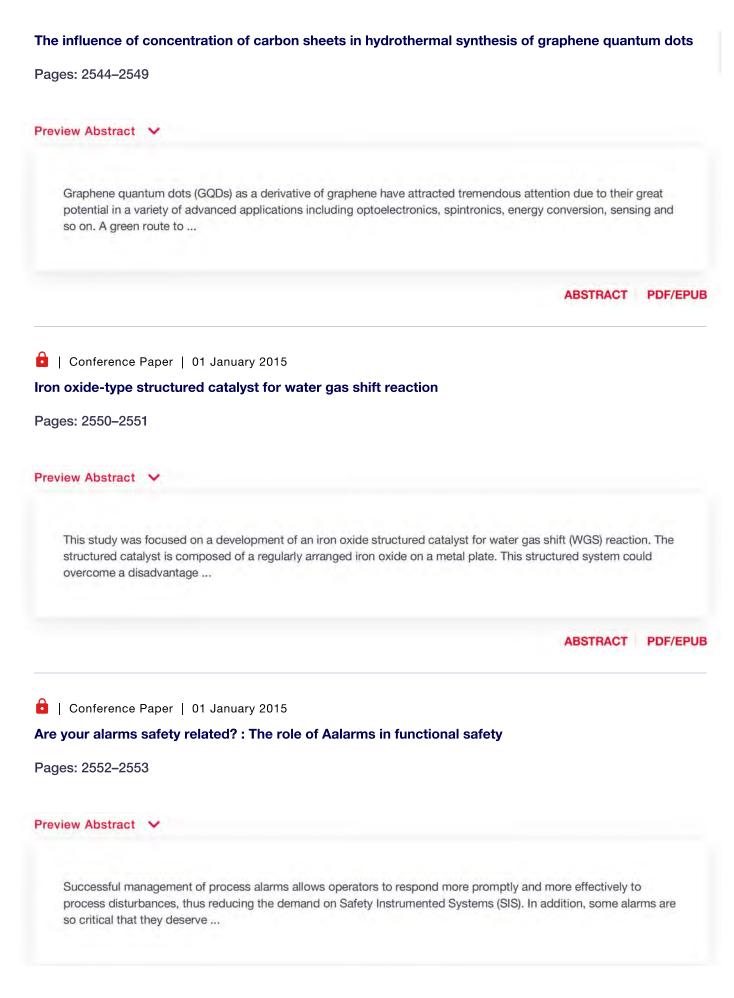


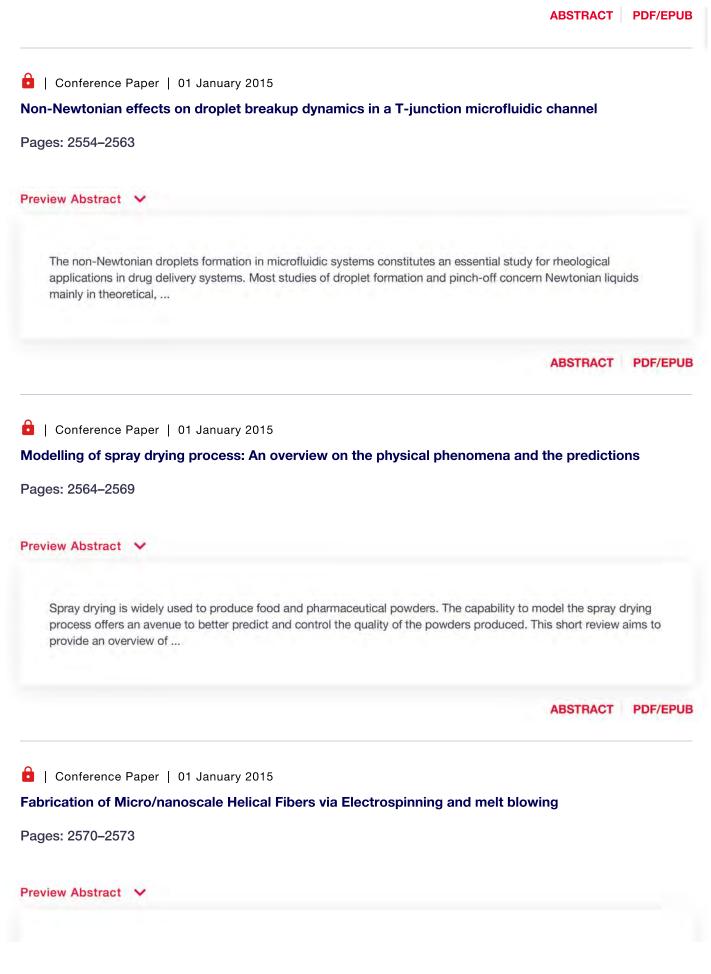


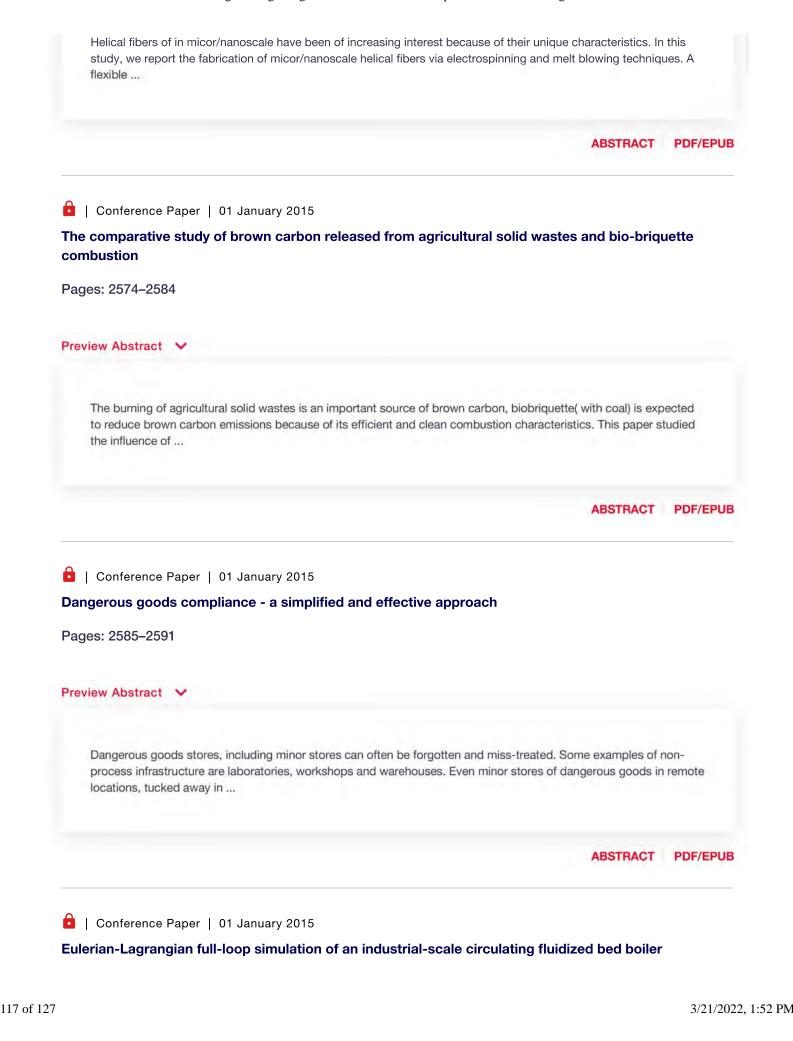


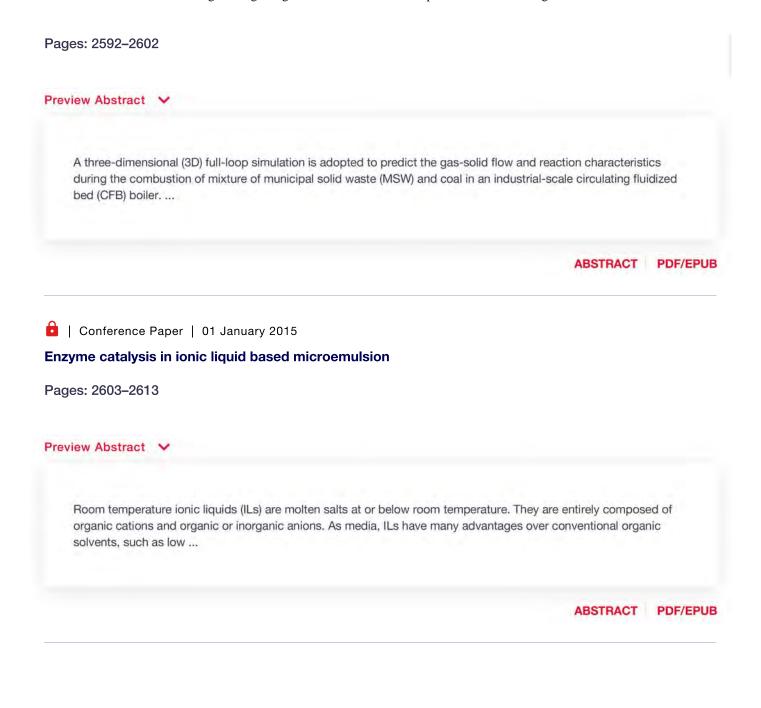


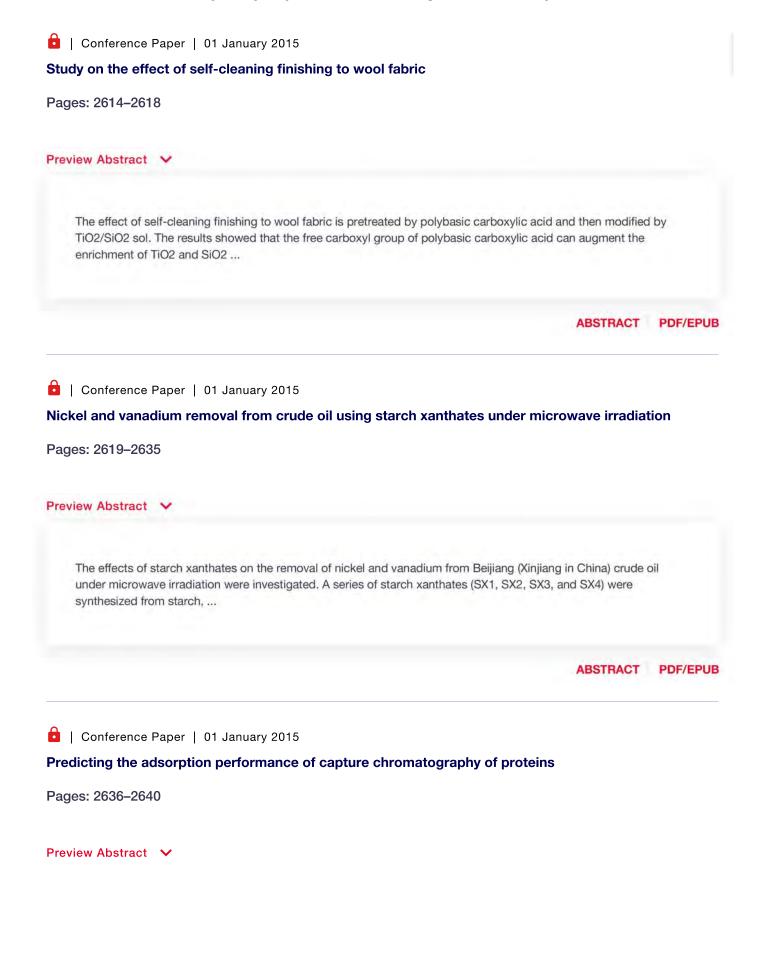


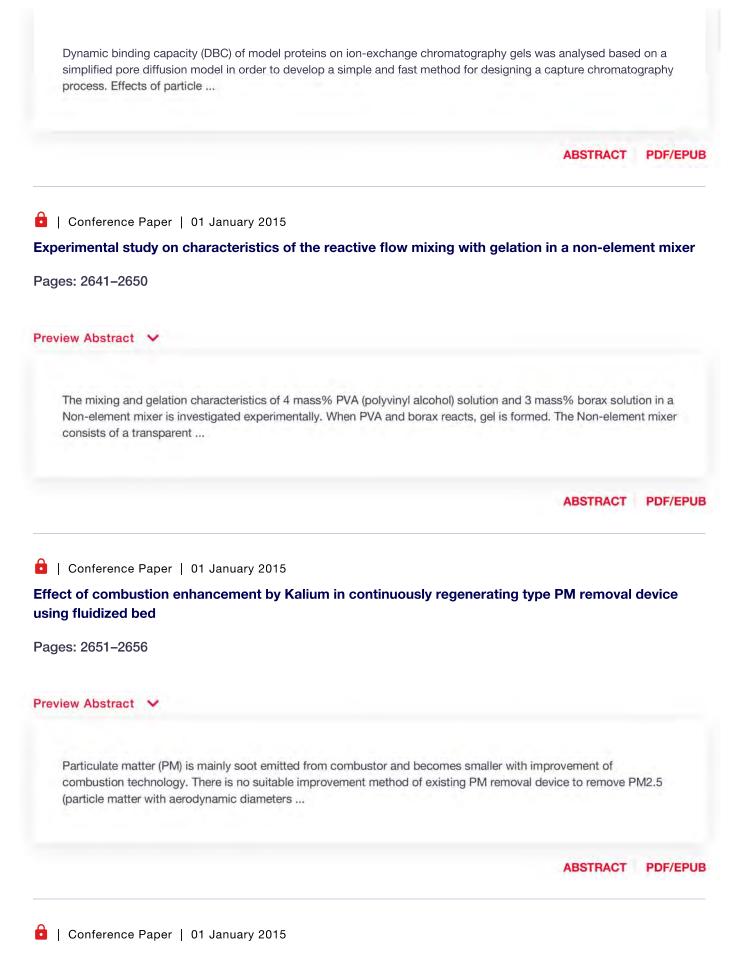


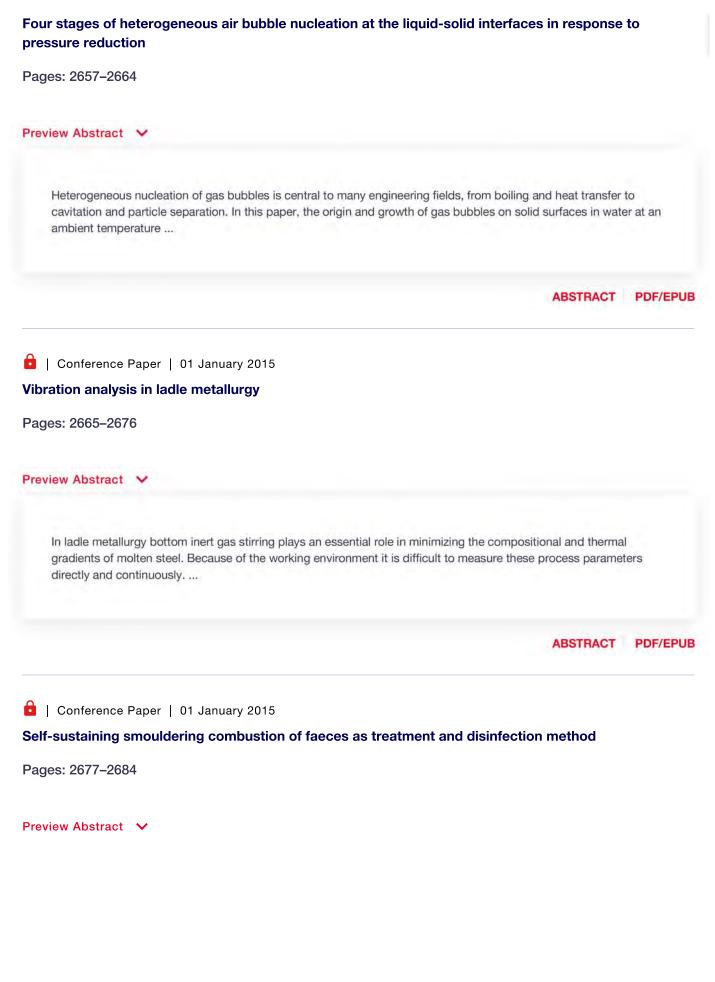


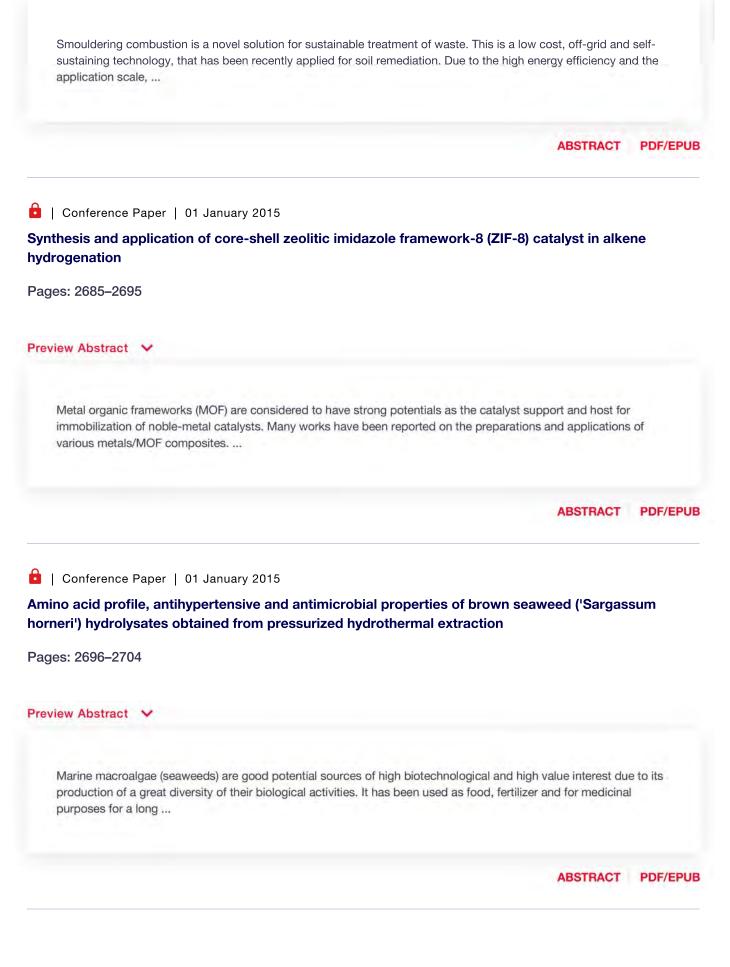


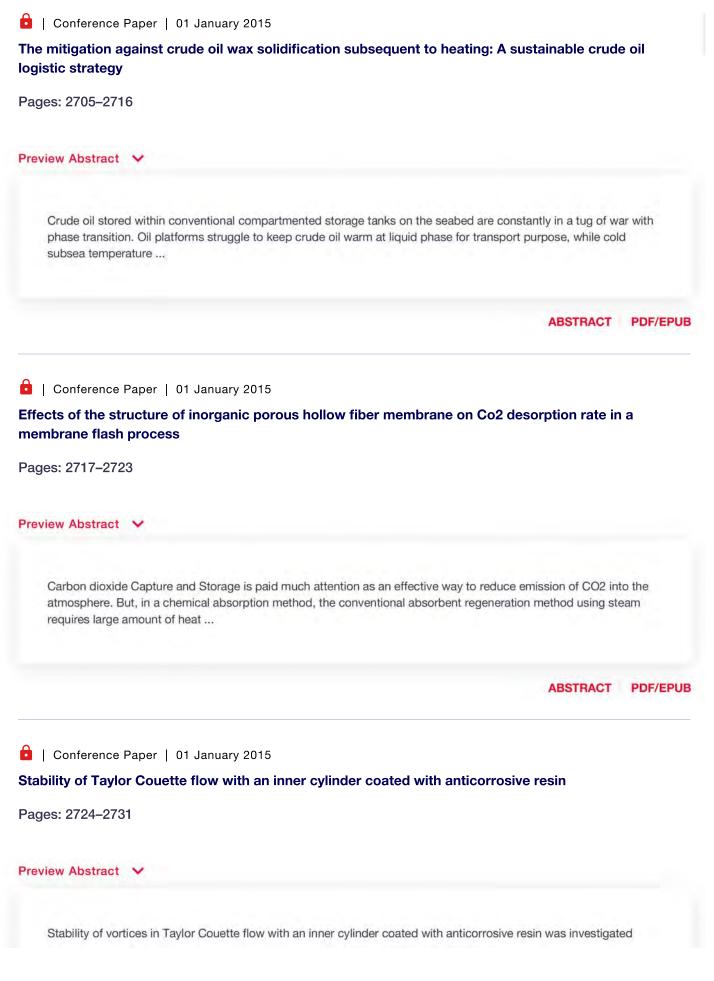


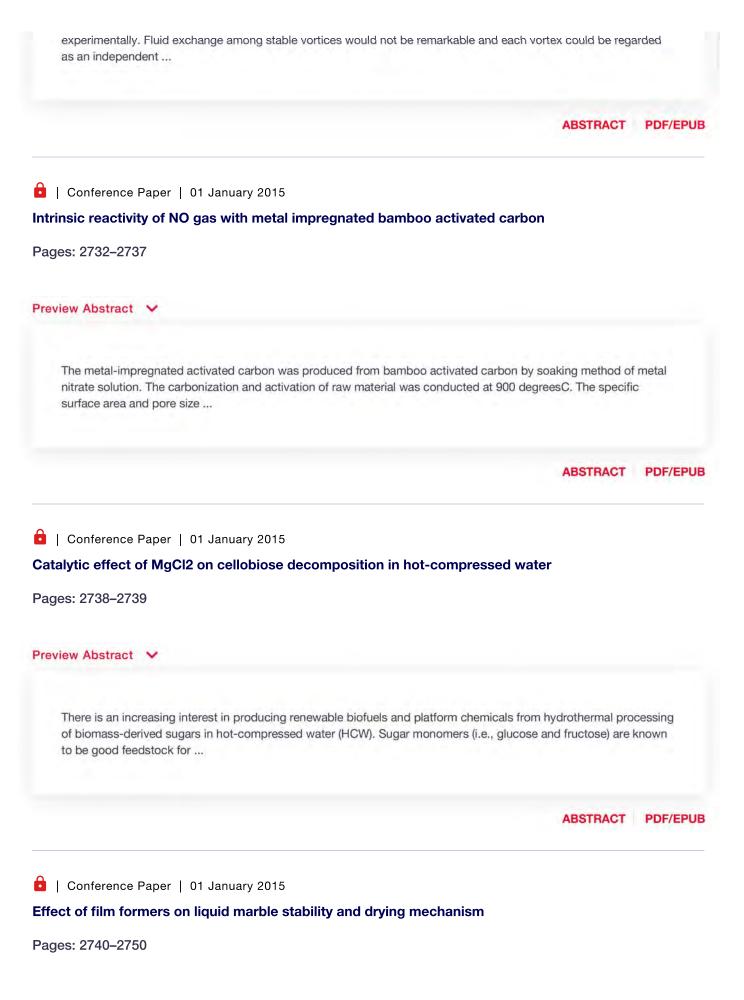


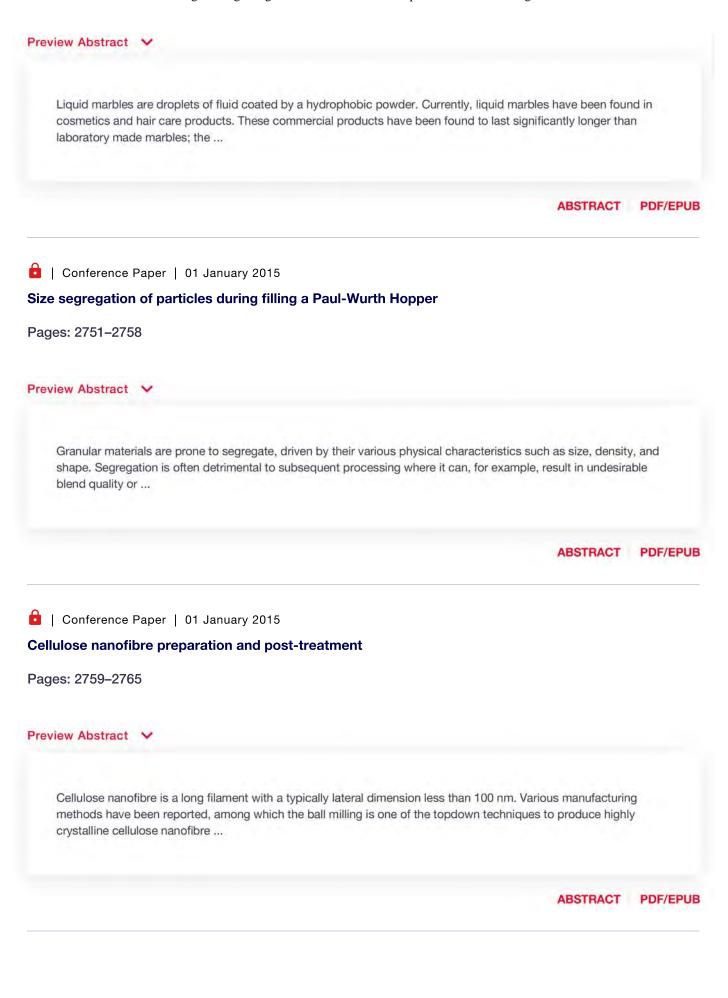












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