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# Biosurfactant Production and Biodesulphurization: Integrated Approach for Fuel Processing

**Rajni Sharma[1], Jagdish Singh[2] and Neelam Verma[1]***

[1]*Department of Biotechnology, Punjabi University, India*

[2]*Department of Biotechnology, Mata Gujri College, India*

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***Corresponding author:** Neelam Verma, Department of Biotechnology, Punjabi University, Patiala-147002, Punjab, India, Tel: +91-175-3046262(O)/+91-175-2285708(R); Fax: +91-175-2283073; Email: verma.neelam2@gmail.com

## Abstract

The ever-growing global energy demand inflicts the incessant fuel supply at affordable rate. The energy from fossil fuels comprises a major (85%) fraction of energy source, though the stocks of these fuels are being depleted and leading energy crisis. It is estimated about 2-4 trillion barrels of crude oil remain entrapped within the reservoirs due to its very high viscosity. Bio surfactants, the microbial products help to improve the mobility of oil by reducing the viscosity and capillary forces retaining the oil inside the reservoir. Biosurfactants being stable at extreme conditions of temperature, pH and salinity simulating the reservoir environment are the important tools for microbial enhanced oil recovery. These molecules have potential to replenish the depleting reservoirs with tremendous quantity of entrapped oil. On the other hand, supply of sulphur-free fuel is crucial for refineries to combat the pollution problem and to meet the stringent environmental regulations. Sulphur dioxide released from the burning of sulphur laden fuel leads to acid rain and air pollution. In the current scenario, Bio-desulphurization (BDS) is a fascinating approach capable of removing complex compounds under mild conditions. The addition of surfactants was found to enhance the BDS rate by improving the solubility of organic compounds to the aqueous media and facilitating the microbes to get better access. Further, the desulphurized products can be converted into the surfactant-like substances subsequently enhancing BDS activity. These two different lines of action, bio surfactant production and bio desulphurization, can work in the integrated manner to improve the recovery of oil and its desulphurization which will reduce the burden from refineries and cut down the operational cost without compromising the environmental safety.

**Keywords**: Biosurfactant; Biodesulphurization; MEOR; Fuel; Energy; Refineries

## Introduction

The global energy demand has been increased due to intense population growth, industrialization and high standard of living. For hundreds of years, fossil fuels have remained the core source of energy and will still remain for many years despite the contribution from other alternative sources like biodiesel, geothermal energy and solar energy [1]. Nevertheless, the recent studies exposed the decline in oil production in some parts of the world due to oilfield maturity and it is difficult to discover new oil fields as an alternative to the exploited oil fields [2].

It is amazing to know that nearly 2-4 trillion barrels of crude oil remain in the reservoirs worldwide after the application of traditional recovery methods due to inability of oil to move out of the rocks due to high viscosity and interfacial tension [3,4]. To recover more oil from the existing and dumped oil fields, attention has been focused on the enhanced oil recovery (EOR) techniques like steam injection, polymer flooding, surfactant flooding or in situ combustion. However, these techniques are highly expensive, high energy demanding, hazardous and environment polluting. Therefore, the use of microbes and their metabolites for the improvement of the oil recovery is an excellent alternate and established as Microbial enhanced oil recovery-MEOR [5]. Biosurfactants are the significant tools for MEOR as these are competent to lower surface tension, viscosity, interfacial tension as well as capillary forces holding the oil within the reservoir. Henceforth, the biosurfactants facilitate the oil recovery by improving the oil mobilization out of the reservoir by forcing it to pump outward [6]. These molecules are produced by a vast variety of microbes (bacteria, yeast and fungi) [7-9].

Conversely, the removal of sulphur from the fuels is mandatory to meet environment legislations. A sulfur limit of 10-15ppm in crude oil was espoused by most of the developed countries while, in India, a sulfur limit of 50ppm is adopted in the metropolitan cities since 2010 [10]. The exploitation of sulphur containing fuel entails rigorous health and environment threats including respiratory and cardiopulmonary diseases and acid rain [10]. At present, the refineries rely on the hydrodesulphurization to remove sulphur which operates at high temperature (200 °C to 425 °C) and pressure (1-18MPa) and insufficient to remove the complex compounds [11]. Biodesulfurization (BDS) is a superb remedy for this predicament allowing the removal of sulphur from complex organo sulphur compounds using microbial potential [12]. The use of surfactants/biosurfactants in BDS process enhances the desulphurization efficiency of microbes by emulsifying the hydrocarbon substrates and desulphurized products possess the surfactant like substances [13,14]. Therefore, the desulphurization process helps to the formation of surfactant and the addition of surfactant facilitate the desulphurization process. The integration of these two processes would outcome the economic and eco-friendly fuel supply.

## Role of Surfactants in Biodesulphurization

Since the bacteria reside in the water phase and the organosulfur compounds dissolve in organic phase, the biodesulfurization reactions occur at the interface. Therefore, the efficiency of the process depends on a sufficient oil/water contact and the transfer of organosulfur compound from the oil bulk phase to the interface [15]. The low desulfurization efficiency examined in some microbes may be attributed to failure of biocatalyst to get access on hydrophobic substrate due to limited mass transfer. A rapid growth was observed with more aqueous soluble $DBTO_2$ as compared to less soluble DBT as sole sulfur source [16]. To alleviate this bottleneck, administration of the surfactant in the desulfurizing media is a very good practice.

The effect of various surfactants including Tween-80, Triton-100X and Brij-35 along with cyclodextrins was investigated on the desulfurization by *Corynebacterium sp*. ZD-1 and improved BDS activity was observed as compared to the activity in their absence. Tween-80 provided the best outcome with DBT mass transfer between aqueous and organic phases [17]. The increase of BDS efficiency of *R. erythropolis* 1awq with Tween-80 was employed due to lower the product inhibition by diffusing it away from the cell during the desulfurization from diesel oil [18]. The BDS process of DBT in model oil by resting cell of *P. putida* CECT5279 was improved by combination of co-solvents and surfactants. The surfactants improved the solubility of hydrophobic substrates in water by reversed micelles formation which enhanced the surface area of oil-water interface which in turn improved the transport of DBT into the cells in aqueous media [19]. The biosurfactants produced by *Staphylococcus* sp. LFA and *B. cereus* SGI were used to enhance the biodesulfurization activity of *Pantoea agglomerans* D23W3 and *Klebsiella sp*. 13T to overcome the limitation of mass transfer [20].

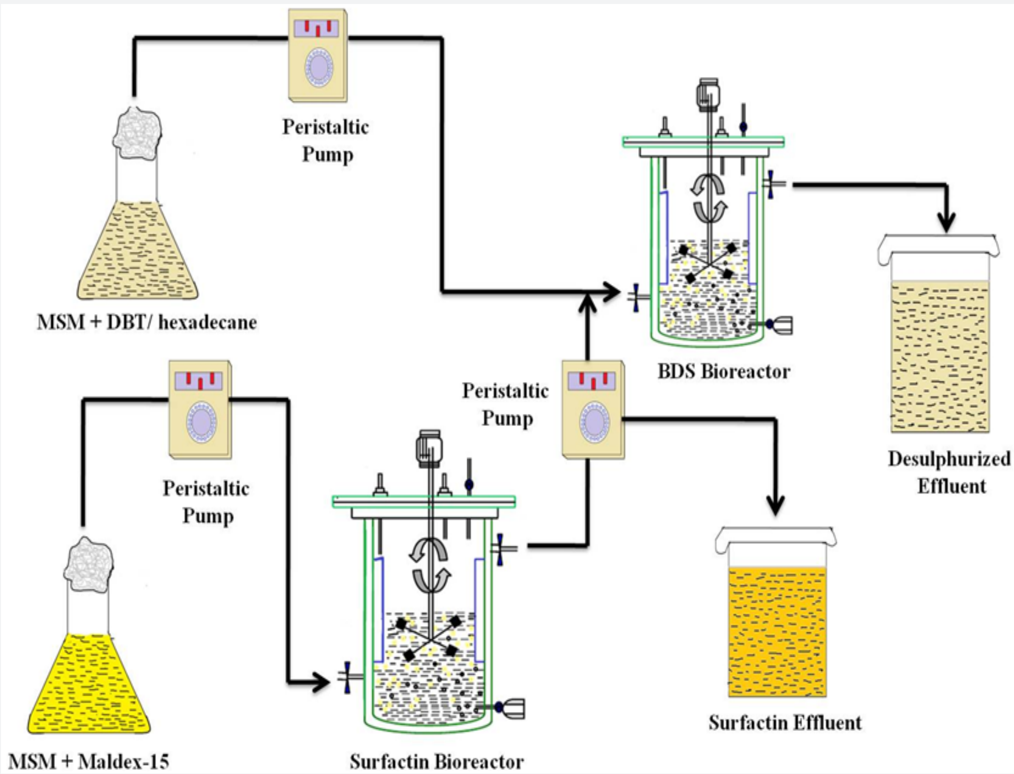


**Figure 1:** Schematic diagram of two-phase bioreactor for BDS and surfactin production.


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A two-phase bioreactor was fabricated by combining two vertical rotating bioreactors (Figure 1) with immobilized cells of *R. erythropolis* and *B. subtilis*. Around 98% biodesulfurization of oil (398mg/L S) was described along with biosurfactant production (4.8g/L). The appropriate quantity of first bioreactor effluent embracing surfactin was blended with influent feed of other containing DBT dissolved in hexadecane and observed the enhanced BDS activity (210.5mM 2-HBP kg $dcw^{-1}$ $h^{-1}$) [21].

The improved desulfurization activity was attained with the use of non-ionic surfactants, Span 80 and Tween 80 [13]. DBT desulfurization by *R. erythropolis* was analyzed for mass transport step by applying biocatalyst in three forms: aqueous phase-free cells, cell aggregates and cells adhered to oil. Mass transfer limitation was found more prominent in the cell aggregates. The agitation imparting power input per volume (P/V) higher than 10,000 $Wm^{-3}$ and/or impeller tip speed greater than 0.67m/s were reported satisfactory to prevail over DBT mass transport in oil-water [22].

## Surfactant Production in biodesulphurization process

Dibenzothiophene (DBT) is represented as a model compound in the crude oil. DBT biodesulphurization may take place via different pathways like kodama pathway and 4S pathway [10]. The DBT degradation via kodama pathway lead to the breakdown of benzene rings lowering calorific value while 4S pathway provides the way to remove sulphur from the organosulphur compounds in a specific way retaining the benzene rings intact [23]. Some researchers attempted to convert the end-products of 4S pathway into commercial products resembling surfactants. To modify the process economics, the conversion of 2-HBP into hydroxyphenyl benzene sulphinate was studied to generate linear alkylbenzene sulphonates like surfactant which also increased the desulfurization rates [24]. In 1999, a patent was granted to Lange and his team providing detailed information on the synthesis of surfactants from the penultimate product of specific 4S pathway (Figure 2). Transformation was executed at hydroxyl group to synthesize esters or by alkylation of the ring. The side chain length could be varied to create either oil- or water-soluble detergents [25]. Other marketable products include hydrotropes, phenolic resins, biocides or adhesives produced by sulfones and sulfoxides and 2-HBP is also renowned industrial biocides [26]. About 80% desulfurization of exhausted engine oil (0.16-1.05% S) in the bioreactor was studied with concomitant production of biosurfactant which consecutively facilitates the desulfurization [14]. Recently, Kilbane & Stark [27] also demonstrated the use of 4S pathway for the production of other chemicals such as surfactants, polythioesters and antibiotics. The surfactants play an important role in the recovery of entrapped oil from the reservoirs [6]. A large number of laboratory scale sand-pack tests [5,28,29] and field tests [30,31] have been performed to check the validity of biosurfactants for oil recovery successfully.

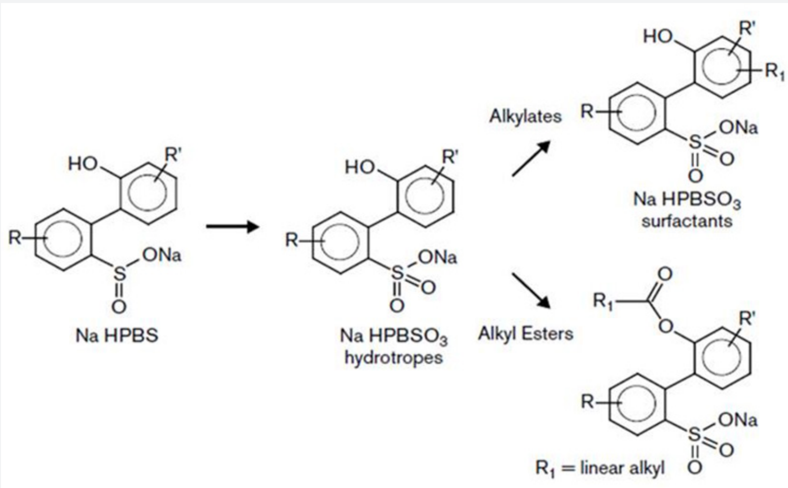


**Figure 2:** Conversion of HPBS (penultimate product of 4S pathway) into marketable surfactants [26].

## Conclusion

The biosurfactant production and biodesulfurization represent the symbiotically integrated approach for recovery of exploitable fuel. The use of microbes and their metabolic products make the process eco-friendly and cost-effective. The biodesulphurization by 4S pathway remove the sulphur resuming the calorific value of fuel with concomitant production of surfactants. In contrast, the addition of surfactants in the desulphurization process enhances the efficiency by making the hydrocarbon substrate available to the biosystem. These mutually beneficial processes open a way for refineries to provide the fuel at affordable rate. An advanced research in this integrated field may help to alleviate the energy crisis in future.

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