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Review

Application of Magnetic Nanoparticles in Bioreactors to Enhance Mass Transfer during Syngas Fermentation

Jude A. Okolie[1], Evelyn Sajeev[2], Sheshank Shekher[3], Chukwuma C. Ogbaga[4,5], Kwaghtaver S. Desongu[6] and Burcu Gunes[2]

[1]Gallogly College of Engineering, University of Oklahoma, Norman U.S.A.
[2]School of Biotechnology and DCU Water Institute, Dublin City University, Glasnevin, Dublin, Ireland
[3]Department of Chemistry, Netaji Subhas University of Technology, Delhi, India
[4]Department of Biological Sciences, Faculty of Natural and Applied Sciences, Nile University of Nigeria, Abuja, Nigeria
[5]Department of Microbiology and Biotechnology, Faculty of Natural and Applied Sciences, Nile University of Nigeria, Abuja, Nigeria
[6]Department of Chemical Engineering, Federal University of Technology, Minna Nigeria.
* Correspondence: jude.okolie@ou.edu

Abstract

Gas-liquid mass transfer is a significant issue in most bioprocesses. More importantly, gas-liquid mass transfer limitation requires further attention during syngas fermentation (SNF). The gas-liquid mass transfer of gaseous substrates (CO, CO_2, and H_2) into the fermentation broth is a rate-limiting step in SNF that leads to low productivity and poor economic feasibility. Enhancing this process during SNF can result in high efficiency, better production of ethanol, as well as lower energy consumption. While pressure and power input are important factors for improving reactor design, adding magnetic nanoparticles (MNPs) in the liquid phase is critical to achieving an enhanced gas-liquid mass transfer. The present study reviewed recent advances in the application of MNPs for an improved gas-liquid mass transfer during syngas fermentation. A brief overview of SNF and the effects of MNPs on SNF process are outlined. In addition, the hydrodynamic effect at the gas-liquid boundary is also seen as a mechanism in which nanoparticles increase mass transfer, and the mechanism is elucidated in detail.

Keywords; Nanoparticles; syngas fermentation; mass transfer; biofuel; bioethanol

1. Introduction

Climate change challenges, elevating world population and the incessant demand for energy have facilitated research in alternative energy resources over the past few years. Thermochemical (e.g. pyrolysis and gasification) and biological processes (e,g anaerobic digestion and syngas fermentation) are promising valorization technologies for the transformation of biogenic waste into green fuels and chemicals [1]. Among the biological process, syngas fermentation (SNF) is a promising technology for the production of lignocellulosic biomass-derived ethanol. SNF is advantageous because it does not require biomass pretreatment. Furthermore, it is a very good alternative to Fischer-Tropsch Synthesis (FT) for the production of liquid hydrocarbon fuels. It has been studied up to an industrial scale over the past few years. Compared to FT, syngas fermentation does not require a fixed CO/H_2 ratio [2]. SNF can be combined with thermochemical processes in a hybrid process which involves the gasification of feedstock to syngas and microbial fermentation of syngas to bioethanol [3].

It took researchers around twenty-five years to commercialize SNF with companies such as LanzaTech Inc. conducting genetic manipulation of *Clostridium autoethanogenum* to produce 1-butanol [4]. Although SNF is fundamentally focused on the *Clostridia* species as the natural host, other microbial platforms such as *E.coli* and *S. cerevisiae* are also suitable for the process. It should be mentioned that the low mass transfer rate in gas-liquid interface is a major issue hindering the implementation of SNF on a large scale [4]. A successful mass transfer for the process requires several key factors such as an efficient bioreactor configuration. However, the process can be mass transfer limited if the rate of mass transfer is not high enough for cell growth demand.

The rate-limiting step in SNF is the gas-liquid mass transfer of the gaseous substrates (CO, CO_2, and H_2) into the fermentation broth. This leads to low productivity and poor economic feasibility of the process [2]. Therefore, a bioreactor configuration that can attain efficient mass transfer and high cell density in an economically feasible manner is essential for SNF. Common reactors such as the continuous stirred tank reactor (CSTR), bubble column, and airlift reactors are widely used in SNF to enhance the mass transfer limitations [5]. Subsequently, the volumetric gas-liquid mass transfer coefficient (kLa) is frequently used as the criterion to measure

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the mass transfer efficiency among various reactor configurations. Furthermore, the gas-liquid mass transfer rate in a fermentation broth is determined by power input, reactor geometry and pressure. Despite examining various reactor designs to improve the performance of syngas fermentation, the process of altering reactor design is limited. New alternative methods such as using nanoparticles (NPs) to increase the gas-liquid mass transfer rates show promising potential to enhance mass transfer in syngas fermentation [4].

Kim et al. [6] tested six types of NPs (palladium on carbon, palladium on alumina, silica, hydroxyl-functionalized single-walled carbon nanotubes, alumina, and iron (III) oxide) to enhance gas-liquid mass transfer during SNF. Their results showed that silica NPs at a concentration of 0.3 wt% showed better enhancement of syngas fermentation [6]. The enhancement of the mass transfer coefficient by the adhesion of NPs to the gas-liquid interface can be explained by three mechanisms: a shuttling or grazing effect, hydrodynamic effects at the gas-liquid boundary layer, and changes in the specific gas-liquid interfacial area [6]. Moreover, an easy and affordable recovery method is necessary to make the process economically feasible. Magnetic nanoparticles (MNPs) are a promising solution to enable easy recovery of the NPs. In another study, Kim et al. [7] evaluated the influence of MNPs on CO, H_2 and CO_2 solubility as well as the acid and alcohol production during SNF [7]. Based on their observations, the magnetic silica nanoparticles with Co and Fe oxides improved the gaseous solubility and production of alcohols and acids compared to the experiments without MNPs.

Owing to the influence of MNPs on SNF, it is important to understand the underlying mechanism. However, there are limited studies in this area. Sun et al. [8] provided a comprehensive review of SNF with a focus on process development but the authors did not discuss the role of MNPs in detail [8]. Recently, Gunes [2] outlined the current status and prospects of biofilm reactors for enhancing higher syngas fermentation yields. Although MNPs were discussed briefly, more information is still lacking in the literature. To fill the knowledge gaps, the present review outlines recent advances in the application of MNPs to improve the gas-liquid mass transfer

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limitations during syngas fermentation. A brief overview of SNF is outlined as well as the effects of MNPs on the syngas fermentation process.

2. Overview of syngas fermentation

SNF is a biochemical process used to convert syngas into green fuels and chemicals with the help of microorganisms in an oxygen-depleted surrounding [9]. Syngas is a flammable gas mixture primarily composed of carbon monoxide (CO), hydrogen (H_2) and carbon dioxide (CO_2). A high temperature or high pressure is not required for syngas fermentation. Moreover, a diverse set of microorganisms can be involved in syngas fermentation with their capabilities of utilizing CO and/or CO_2/H_2 as the metabolic building block (Table 1). The bacteria primarily used in syngas fermentation belong to a group of prokaryotic single cell organisms termed “acetogens”. Acetogens use the acetyl-CoA pathway for reductive synthesis of acetyl-CoA from CO, and/or CO_2 and H_2 [10]. This pathway is also known as the Wood-Ljungdahl pathway. Acetogenic bacteria convert CO, H_2 and CO_2 derived from biomass or waste materials into acetic acid. Furthermore, acetyl-CoA is an intermediate metabolite in the Wood–Ljungdahl biochemical pathway that is converted to synthesize cell mass, and complex chemicals and yields organic acids and alcohols i.e., acetic acid and ethanol. Acetic acid can be released from the cell or reduced through acetaldehyde to ethanol as seen in Figure 1[11].

The first acetogen discovered to produce ethanol from syngas was *Clostridium ljungdahlii* and acetogenic alcohol producers such as *C. autoethanogenum* and *C. carboxidivorans*. They have also been shown to synthesize butanol and hexanol [10]. It should be emphasized that commercial-scale syngas fermentation needs a microbial biocatalyst with specific traits such as high substrate utilisation, high product yield, high product selectivity, low product inhibition, prolonged metabolic viability and environmentally safe [7].

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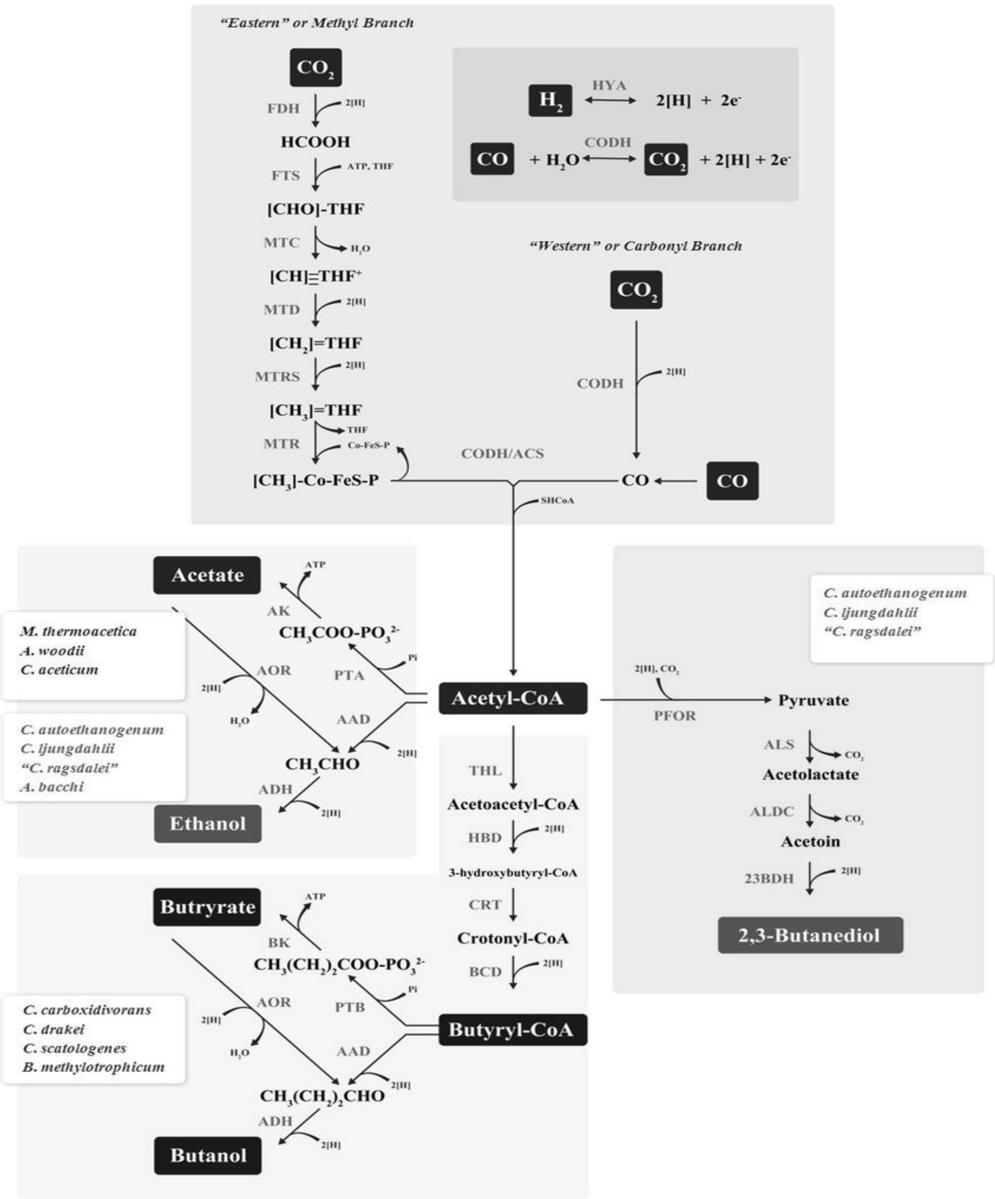

Figure 1: An overview of the Wood-Ljungdahl pathway. Adapted from [11].

Table 1: Overview of different microorganisms used in the conversion of syngas into fuels and chemicals via syngas fermentation [5].

Mesophilic bacteria (acetogen)	**Substrate**	**T OPT (°C)**	**pHOPT**	**Products(s)**
Acetobacterium woodii	CO_2/H_2, CO	6.8	30.0	Acetate

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Acetogenium kivui	CO_2/H_2, CO	6.6	NA	Acetate
Acetonema longum	CO_2/H_2	30 - 33	7.8	Acetate, *n*-butyrate
Alkalibaculum bacchi	CO_2/H_2, CO	37	8.0-8.5	Acetate, ethanol
Peptostreptococcus productus	CO_2/H_2, CO	37	7.0	Acetate
Butribacterium methylotrophicum	CO_2/H_2, CO	37	5.5 – 7.4	Acetate, ethanol, *n*-butyrate, *n*-butanol
Clostridium aceticum	CO_2/H_2, CO	30	8.3	Acetate
Clostridium autoethanogenum	CO_2/H_2, CO	37	5.8 – 6.0	Acetate, ethanol, lactate, 2,3-butanediol
Clostridium carboxidivorans P7	CO_2/H_2, CO	37	5.8 – 6.2	Acetate, ethanol, *n*-butyrate, *n*-butanol, lactate
Clostridium drakei	CO_2/H_2, CO	25 - 30	5.8 – 6.9	Acetate , ethanol, , *n*-butyrate
Clostridium formicoaceticum	CO	37	NA	Acetate, formate
Clostridium glycolicum	CO_2/H_2	37 - 40	7.0 – 7.5	Acetate
Clostridium ljungdahlii	CO_2/H_2, CO	37	6.0	Acetate, ethanol, lactate, 2,3-butanediol
Clostridium magnum	CO_2/H_2	30-32	7.0	Acetate
Clostridium mayombei	CO_2/H_2	33	7.3	Acetate
Clostridium methoxybenzovorans	CO_2/H_2	37	7.4	Acetate
Clostridium ragsdalei P11	CO_2/H_2, CO	37	6.3	Acetate, ethanol, lactate, 2,3-butanediol
Eubacterium limosum	CO_2/H_2, CO	38-39	7.0-7.2	Acetate
Oxobacter pfennigii	CO_2/H_2, CO	36-38	7.3	Acetate, *n*-butyrate

2.1 Effect of process parameters on syngas fermentation

SNF temperature plays a crucial role in cell metabolism and growth. Temperature affects the solubility of CO, H_2, and CO_2 in the liquid bulk. The optimum temperature for microorganisms varies in syngas fermentation as seen in Table 1. Similarly, the pH of the media has a significant impact on metabolic processes, cell growth and product distribution. The optimum pH for microorganisms can be seen in Table 1. pH shift has also been proven to be an effective strategy to promote ethanol production [12].

Richter et al [13] conducted a two-stage fermentation using *C.ljungdahlii* with two reactors for better ethanol production. The system comprised of a 1L CSTR for growth and a 4L bubble column for ethanol production. Reactor A had a pH of 5.0 and Reactor B had 4.0-4.5. This pH shift resulted in a thirty fold improvement in ethanol productivity compared to a single CSTR which uses *C.ljungdahlii* [13]. This is because the temperature and pH can be fixed separately in each stage. Furthermore, the working volume of Reactor A and Reactor B can be changed to various growth and dilution rates to promote rapid growth and acidogenesis [13].

Syngas composition is also vital during SNF. Many microorganisms can use CO as the only carbon and energy source. However, it is believed that syngas fermentation with the presence of H_2 can be beneficial for biofuel production. This is because electrons and protons required for the acetyl-CoA pathway could be obtained from H_2 oxidation via hydrogenase or through oxidation of CO by the CODH enzyme. Excess H_2 has been shown to improve ethanol production in *C. ljungdahlii* culture [14]. Syngas produced from biomass conversion processes could also contain several impurities such as sulphur gas, ethane, tar, ethylene and char (Reference(s). These impurities negatively impact syngas fermentation through cell dormancy, inhibition of hydrogenase, and cell growth. Consequently, chemical absorbing units such as sodium hydroxide, sodium hydrochloride and potassium permanganate can mitigate the negative impacts of syngas impurities.

2.2 Mass Transfer issues during syngas fermentation

The current difficulties of mass transfer in biological systems are the low solubility of synthesis gas components in gas-liquid mass transfer. This is due to the fact that each biological system is different. Microorganisms have an array of physiochemical and

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biological differences. Some are filamentous while some can grow branched or dispersed. Some microbes can also increase density and viscosity with time. The mass transfer usually takes place in more than one phase [5].

The volumetric mass transfer (k_{La}) is a parameter that characterizes the mass transfer properties in bioreactors. kLa is dependent on the bioreactor type and geometry, liquid and gas velocities and fluid properties. In a bioreactor, gas hold-up determines the residence time of the gas in the liquid. Similarly, the bubble size can also influence the gas-liquid interface available for mass transfer. In addition, gas holdup impacts the bioreactor design as the design volume of a bioreactor ultimately depends on the maximum gas holdup that can be accommodated [15]. Moreover, an increase in gas hold-up increases the available area for mass transfer. An increase in the superficial gas velocity in the riser increases the liquid velocity which in turn decreases the thickness of the gas-liquid boundary layer decreasing the mass transfer resistance [11].

The current limitation in mass transfer means it is not high enough to meet the rate of cell growth. Mass transfer limitation makes the availability of substrate too low to be consumed by microbes resulting in low productivity. Traditionally, two approaches are usually employed to enhance k_{La} values of syngas constituents' gases. Increasing the specific syngas flowrate (i.e., high supply rate) and enhancing the gas-liquid interfacial area by rising the agitation speed [16].

It is noted that agitation and gas flow rates are inversely proportional to power-per-volume. In a study conducted in CSTR, a common bioreactor, syngas fermentation used these two methods. Two microorganisms were suspended in the fermentation broths as biocatalysts. They increased the specific CO flow rate from 0.14 to 0.86 (gas volume flow per unit of liquid working volume per minute) and increased the agitation speed from 200 to 600 rpm. These changes elevated the k_{La} in the CSTR from 10.8 hr^{-1} to 15.5 hr^{-1} [16]

Unfortunately increasing the agitation is not economically feasible for commercial-scale reactors because of extreme, high energy costs. Likewise, increasing syngas flow rate causes wastage of gaseous substrate and results in shear stress to the microorganisms.

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Moreover, at a high range of flow rate, the syngas supply could exceed the cells' maximum capability of syngas utilization. Subsequently, the flow rate is also dependent on the type of bioreactor used [4].

3. Nanoparticles classification of synthesis method

Nanotechnology has diverse applications and is defined as science at the nanoscale. NPs are particles that are 1- 100 nanometers in diameters and are predominantly applied in areas such as energy and biomedicine. They are "the building blocks" of nanotechnology [17,18]. Interestingly, NPs are now studied to enhance mass transfer in microbiological processes such as syngas fermentation. This is regarded as a promising strategy to increase mass transfer rates as it provides a large surface area for bacteria and holds the potential to increase the interactions between the liquid and the gas phase [17].

There are different methods of preparing NPs which are broadly classified into top-down methods and bottom-up methods [18]. These methods, which are primarily distinguished by their starting material, tend to tremendously influence the morphology (shape and size) of the nanomaterials formed, as well as their functionalities. In top-down methods, particles of bulk materials are broken into nanoparticles of desired properties and morphology using synthesis techniques like chemical etching, laser ablation, mechanical milling, sputtering, and electro-explosion [19,20]. However, in the bottom-up methods, nanoparticles are synthesized from smaller particles like atoms and molecules, which act as building blocks [18]. Bottom-up methods include supercritical fluid synthesis, spinning, sol-gel process, laser pyrolysis, chemical vapour deposition, molecular condensation, chemical reduction and green synthesis [19].

Specifically, magnetic nanoparticles (MNPs) have unique properties that make them fit for various applications in areas such as catalysis, biomedicine, magnetic fluids, data storage, environmental remediation, spintronics, and magneto-resistance sensors [19]. The properties of MNPs include high surface-area-to-volume ratio, quantum properties, and the ability to carry other compounds, such as drugs, due to their small size. Magnetic fields, whose effectiveness depends on the particle magnetic moment and the field gradient, can be used to manipulate the properties of MNPs to make them suitable for many applications [21,22]. The best performing magnetic nanoparticles, depending on the material, have sizes around 10-20 nm because the particle becomes a single domain and exhibits superparamagnetic behaviour beyond a temperature called the blocking temperature [22]. This, however, also results in intrinsic instability over longer periods of time and loss of magnetism that is caused by the oxidation of naked metallic nanoparticles, which are chemically highly active [21,22]. Spherical and cubic magnetic nanoparticles, in particular, have unique desirable properties that have made them objects of much interest [9]. Magnetic nanoparticles can be classified into transition or rare-earth metals, alloys, and oxides. Transitions metals include Fe, Ni, Co, Gd and so on; alloys include Fe-Co, Fe-Ni, Fe-Ni-Mn, Fe-Pt, and so on; Oxides include Fe_3O_4, Fe2CoO4, $Fe_2Mn_xZn_{1-x}$Fe4, etc [23]. The most common and useful magnetic materials are based on metal oxides such as iron (Fe), cobalt (Co), and nickel (Ni). However, these have not been fully studied because they have very active surfaces at the nanoscale [23]. To date, iron oxide is the most used magnetic nanomaterial and, therefore, has captured the attention of many scientists and engineers [24]. For example, Fe_3O_4 NPs are used in separation technology, catalysis, protein immobilization, medical science, and the environment [25].

4. Application of nanoparticles during syngas fermentation

In biofuel production by SNF, nanomaterials can influence the biochemical conversion process by influencing the enzymatic activity or through the improvement of the rate of liquid-gas mass transfer [26]. Kim et al. [6] applied six different types of nanomaterials to improve the mass transfer during syngas fermentation, discovered that the mass transfer of CO, CO_2 and H_2 were enhanced by 272.9%, 200.2% and 156.1% respectively. The authors confirmed from their study that enhancement of mass transfer through the application of nanoparticles could improve the productivity of fermentation using syngas substrates. In another study, some researcher applied methyl functionalized silica and methyl-functionalized cobalt ferrite-silica ($CoFe_2O_4$@SiO_2-CH_3) nanoparticles to improve the mass transfer between syngas and water, with the latter showing better improvement. The authors discovered from the study that both nanoparticles did not only improve significantly the rate of mass transfer between syngas and water, they also

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maintained their capability to enhance mass transfer after being reused up to five times [7]. In addition, nanoparticles such as spherical MCM41 and functionalized silica nanoparticles have demonstrated ability to improve volumetric mass transfer coefficient [27,28].

It is also worthy mentioning that the use of nanoparticles in syngas fermentation also influence the product distribution. For instance, MCM41 nanoparticles were found to enhance H_2 concentration in the product of syngas fermentation using *Rhodospirillum rubrum* [29]. Table 2 provides a summary of key findings of past research on the applications of nanomaterials for syngas fermentation.

Table 2: An overview of prevuous studies on the Application of nanomaterials for syngas fermentation

References	Key Findings
Kim and Lee. [7]	The authors compared two types of nanomaterials, methyl-functionalized silica and methyl-functionalized cobalt ferrite-silica ($CoFe_2O_4@SiO_2$-CH_3), in the fermentation of syngas by Clostridium ljungdahlii for bioethanol production. The latter showed a better ability to enhance syngas-water mass transfer and more efficient productivity. Both nanomaterials maintained their capability to increase mass transfer after being recovered and reused up to five times.
Kim et al. [6]	Six types of nanomaterials were tested for bioethanol production through syngas fermentation. They include palladium of carbon, palladium alumina, silica, hydroxyl functionalized single-walled carbon nanotubes, alumina, and iron (III) oxide, out of which silica nanoparticles at 0.3 wt % offered better enhancement of mass transfer and increased the level of biomass, ethanol and acetic acid production.

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Zhu et al. [29]	The authors added the MCM41 nanoparticles with or without mercaptopropyl functional groups to syngas fermentation reactors. This facilitated the fermentation of CO using Rhodospirillum rubrum and enhanced the concentration of H_2 in the product gas. The yield of H_2 was enhanced by about 200% at 0.6 wt% of the MCM41 nanoparticles
Zhu et al. [28]	Spherical MCM41 nanoparticles were designed to enhance volumetric mass transfer coefficient (kLa) for the fermentation of syngas. These nanoparticles showed a higher value of kLa than silica particles, with surface hydroxyl groups playing a vital role in the kLa enhancement. Mercaptan groups grafted to MCM41 enhanced the kLa by about 1.9 times more than when nanoparticles are not used.
Jeon et al. [27]	Authors synthesized silica and methyl functionalized silica nanoparticles which enhanced the CO_2/water mass transfer system. The volumetric mass transfer coefficient increased by 31% and 145% respectively for each of the nanomaterials, resulting in increased production of bioethanol from fermentation using Chlorella Vulgaris.
Jack et al. [30]	Effluent from CO_2 electrolyzer was connected to a bioreactor where the blend of CO_2 and CO was converted to acetate and ethanol by Clostridium ljungdahlii at rates of 17.87 ± 7.1 and 3.23 ± 1.4 mg/L/h respectively, under autotrophic conditions. These production rates were respectively increased by 217% and 224% by the addition of mercapto-modified silica nanoparticles.

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Gupta and Chundawat [31]	Biologically synthesized ZnO nanoparticles were used to catalyze bioethanol production by the fermentation of sugar obtained from rice straw. A maximum ethanol yield of 0.0359 g/g of dry weight-based plant biomass was produced at a 200 mg/L concentration of ZnO nanoparticle.
Sanusi et al. [22]	The authors examined the effect NPs inclusion at different stages of the instantaneous saccharification and fermentation of waste potato peels. NiO nanobiocatalysts inclusion at pre-treatment stage resulted in a 1.60-fold increase in bioethanol concentration and 2.10-reduction in acetic acid concentration.

5. Conclusions

Syngas fermentation is apromising biological process for the production of biofuels because it does not require biomass pretreatment. Also it is a feasible alternative to Fischer–Tropsch Synthesis (FT) for the production of liquid hydrocarbon fuels. Syngas fermentation is a major topic among researchers both experimental and modelling. Inn addition, it has been studied up on a commercial scale over the past few years. Compared to FT, syngas fermentation can proceed effectively without a fixed CO/H_2 ratio. Several studies have been carried out to circumvent the issues of syngas fermentation, including poor mass transfer issues, low gas solubility, and low productivity. The gas-liquid mass transfer of gaseous substrates (CO, CO2, and H2) into the fermentation broth is a rate-limiting step in SNF that leads to low productivity and poor economic feasibility. The addition of magnetic nanoparticles (MNPs) in the liquid phase helps to address the gas- liquid mass transfer limitations thereby achieving an enhanced gas-liquid mass transfer. This mini review summarizes advances in the application of MNPs for improving syngas fermentation. An overview of syngas fermentation process as well as the effect of different operatign paramters are briefly disucssed. Previous studies in MNPs enhanced syngas fermentation are also reviewed.

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