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Review

Biomass-derived syngas fermentation into biofuels: Opportunities and challenges

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ABSTRACT

The conversion of biomass-derived synthesis gas (or syngas in brief) into biofuels by microbial catalysts (such as *Clostridium ljungdahlii*, *Clostridium autoethanogenum*, *Acetobacterium woodii*, *Clostridium carboxidivorans* and *Peptostreptococcus productus*) has gained considerable attention as a promising alternative for biofuel production in the recent past. The utilization of the whole biomass, including lignin, irrespective of biomass quality, the elimination of complex pre-treatment steps and costly enzymes, a higher specificity of biocatalysts, an independence of the H_2:CO ratio for bioconversion, bioreactor operation at ambient conditions, and no issue of noble metal poisoning are among the major advantages of this process. Poor mass transfer properties of the gaseous substrates (mainly CO and H_2) and low ethanol yield of biocatalysts are the biggest challenges preventing the commercialization of syngas fermentation technology. This paper critically reviews the existing literature in biomass-derived syngas fermentation into biofuels, specifically, different biocatalysts, factors affecting syngas fermentation, and mass transfer. The paper also outlines the major challenges of syngas fermentation, key performance index and technology road map, and discusses the further research needs.

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1. Introduction

Lignocellulosic biomass is considered as a renewable feedstock, and is the most abundant carbohydrate on Earth. The US has the potential to produce nearly 1.3 billion dry tons of biomass annually which could displace as much as one-third of current transportation fuel demands (USDA and USDOE Joint Report, 2005).

Currently, biofuels are commercially produced from sugar, starch and oil-seed based feedstocks. For example, bioethanol is produced from corn starch in the United States, cassava starch in Thailand (Nguyen et al., 2007), and cane sugar in Brazil (Schubert, 2006). Soybean, palm fruits, and rape and canola seeds are the common feedstocks for biodiesel production (Demirbas, 2007). The further expansion of biofuel production from many of these feedstocks, however, triggers debate on food/feed versus fuel. Thus, for sustainable biofuel production, non-food feedstock should be used. Lignocellulosic biomass such as agri-residues (e.g., corn stover, wheat and barley straws), agri-processing byproducts (e.g., corn fiber, sugarcane bagasse, seed cake, etc.), and energy crops (e.g., switch grass, poplar, banagrass, miscanthus, etc.) do not compete with food and feed, and is considered to be renewable feedstocks for biofuel production.

There are two major pathways for producing biofuel, especially ethanol from lignocellulosic biomass, namely biochemical and thermochemical pathways. During biochemical conversions, the biomass is subjected to acid, alkaline or steam explosion pre-treatments to break the cellulose–hemicellulose–lignin interactions. These pre-treatments make the biomass more accessible to enzymes. The pretreated biomass is subjected to enzyme hydrolysis to obtain fermentable sugars. The hydrolyzate obtained is then fermented to ethanol (Sun and Cheng, 2002). Biochemical routes, however, face several challenges such as high pre-treatment and enzyme costs, low fermentability of mixed sugar stream (especially 5-carbon sugars), the generation of inhibitory soluble compounds (e.g., acetic acid, furfural, 5-hydroxymethylfurfural, phenolic compounds, etc.) and the degradation of sugars (García-Aparicio et al., 2006). On the other hand, thermochemical pathways involve the gasification of biomass into synthesis gas or syngas (a mixture of CO and H_2), and then converting the syngas to biofuels by using chemical catalysts known as Fischer–Tropsch (FT) process or by using microbial catalysts known as syngas fermentation.

Chemical catalytic conversion of syngas to ethanol has been studied since 1920's using homogeneous and heterogeneous chemical catalysts (Subramani and Gangwal, 2008). Though, both these catalytic processes have higher selectivity to ethanol, higher operational and catalysts cost make these processes unattractive for commercial applications. Further, the modified methanol synthesis and FT synthesis based on CuZn, CuCo and MoS_2 have been evaluated in syngas conversion into alcohols and the rate of ethanol production was significantly lower than those achieved in

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methanol synthesis (Spivey and Egbebi, 2007; Subramani and Gangwal, 2008).

The syngas fermentation into ethanol and other bioproducts is considered to be more attractive due to several inherent merits over the biochemical approach and the FT process (Bredwell et al., 1999; Brown, 2003; Heiskanen et al., 2007; Klasson et al., 1990), such as (a) utilization of the whole biomass including lignin irrespective of the biomass quality; (b) elimination of complex pretreatment steps and costly enzymes; (c) higher specificity of the biocatalysts; (d) independence of the H_2:CO ratio for bioconversion; (e) aseptic operation of syngas fermentation due to generation of syngas at higher temperatures; (f) bioreactor operation at ambient conditions; and (g) no issue of noble metal poisoning.

Biological catalysts (such as *Clostridium ljungdahlii*, *Clostridium autoethanogenum*, *Acetobacterium woodii*, *Clostridium carboxidivorans* and *Peptostreptococcus productus*) are able to ferment syngas into liquid fuel more effectively than the use of chemical catalysts (e.g., iron, copper or cobalt) (Heiskanen et al., 2007; Henstra et al., 2007). The major drawbacks of the chemical catalytic process are the low specificity, high operating temperature and pressure, need of maintaining constant feed gas composition and high sensitivity to toxic gases (Phillips et al., 1994; Vega et al., 1990; Worden et al., 1991).

Syngas fermentation has also several limitations such as low productivity and poor solubility of gaseous substrates in the liquid phase. These limitations are thus preventing the commercialization of the syngas fermentation technology. This paper critically reviews the existing literature on biomass-derived syngas fermentation into ethanol. Furthermore, relevant background information including pathways, microbial aspects, mass transfer and factors affecting syngas fermentation are also briefly discussed. In addition, the challenges, some of the key performance indices, future research directions, and a technological road map are also included.

2. Syngas conversion to ethanol

The catalytic conversion of syngas to hydrocarbons and alcohols by Fisher–Tropsch (FT) synthesis was invented in 1923 by German scientists Franz Fisher and Hans Tropsch (Demirbas, 2007). During energy embargo of 1970's, the conversion of syngas to higher alcohols by FT synthesis appeared as a potential alternative to crude oil (Stelmachowski and Nowicki, 2003). In 1987, *Clostridium ljungdahlii*, a rod shape, gram-positive anaerobic bacteria was discovered which was found to have an ability to ferment carbon monoxide and hydrogen into ethanol and acetic acid. Since then, there has been significant development in syngas fermentation research, especially in process microbiology with discovery of over dozens of new species and process engineering such as new reactor design for improved mass transfer among others (Lynd, 2008).

Gasification of lignocellulosic biomass at a high temperature (750–800 °C) produces a gas mixture containing carbon monoxide (CO), hydrogen (H_2), methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2) and some higher hydrocarbons commonly known as producer gas (Datar et al., 2004). The overall gasification process is endothermic, that is, it requires heat-energy input to drive the process. The composition of producer gas depends on the types of gasifier and biomass, and the gasification conditions among others. Table 1, summarizes the constituents of the gas produced from different gasifiers under different gasification conditions. The synthesis gas predominantly contains H_2 and CO, and is commonly known as syngas in short. After gasification, the syngas mixture passes through a series of filters to remove undesirable pollutants such as tar and solid particles. The purified syngas is converted into liquid fuels by microbial catalysts.

3. Fundamental aspects of syngas fermentation

Syngas-fermenting microorganisms use acetyl-CoA pathway to produce ethanol, acetic acid and other byproducts such as butanol and butyrate from syngas. The electrons required for the conversion is supplied by H_2 and CO, via the hydrogenase and carbon monoxide dehydrogenase enzymes, respectively (Ahmed and Lewis, 2007). In addition, bifunctional carbon monoxide dehydrogenase enzyme produces CO_2 from CO which serves as a carbonyl group to produce acetyl-CoA (Henstra et al., 2007).

Acetyl-CoA serves as a precursor for cell macromolecules as well as an adenosine triphosphate (ATP) source. The overall reductive acetyl-CoA pathway is an irreversible, non-cyclic pathway which occurs under a strict anaerobic environment. There are two major steps involve in the production of acetyl-CoA. During the first step, CO or CO_2 is reduced to a methyl group through a series of reductive reactions in the presence of hydrofolate dependent enzymes and in the expense of ATP. Secondly, the methyl, carbonyl and the CoA groups are combined by the enzymes acetyl-CoA synthase (ACS) and carbon monoxide dehydrogenase complex (CODH) to produce acetyl-CoA (Henstra et al., 2007; Ragsdale, 1991). Acetyl-CoA is further reduced to acetate, ethanol and other byproducts during the later stages of the pathway. The overall biochemical reactions that take place in the reductive acetyl-CoA pathway are shown in Eqs. (1)–(4).

$$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2 \quad \Delta H = -217.9\ \text{kJ/mol} \tag{1}$$

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \quad \Delta H = -97.3\ \text{kJ/mol} \tag{2}$$

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \quad \Delta H = -154.9\ \text{kJ/mol} \tag{3}$$

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \quad \Delta H = -75.3\ \text{kJ/mol} \tag{4}$$

According to Eq. (1), one-third of the carbon from carbon monoxide is converted to ethanol and the combination of the two reactions in Eqs. (1) and (2) indicates that two-third of the carbon from

Table 1
Gas compositions of different gasification processes.

Gasifier type	Fluidized bed air blown	Updraft air blown	Downdraft oxygen blown	Fluidized bed (switchgrass)	Fluidized bed (bark)	Fluidized bed (coal)
N_2 (%)	50	53	3	57	42.9	1
CO (%)	14	24	48	15	19.6	67
CO_2 (%)	20	9	15	17	13.5	4
H_2 (%)	9	11	32	5	20.2	24
CH_4 (%)	7	3	2	6	3.8	0.02
H_2S (%)	n/a	n/a	n/a	n/a	Very low	1
Tars (g/m^3)	<10	>10	1	<1	<1	0
NH_3 (%)	n/a	n/a	n/a	n/a	n/a	0.04
H_2O (%)	n/a	n/a	n/a	n/a	Dry	3
Dust	High	Low	Low	n/a	n/a	n/a
H_2/CO	0.64	0.46	0.67	0.34	1.0	0.36
References	Bridgwater (1995)	Bridgwater (1995)	Bridgwater (1995)	Datar et al. (2004)	Subramani and Gangwal (2008)	

CO can theoretically be converted to ethanol. Similarly, 50% of the carbon from CO can theoretically be converted into acetic acid (Eq. (3)). The overall yield of the fermentation is dependent on the composition of the syngas, where H_2 plays an important role. In this case, H_2 supplies H^+ ions and electrons required in the conversion of syngas into ethanol under the enzymatic activity of the hydrogenase enzyme. If the hydrogenase enzyme is inhibited, the microbes cannot utilize H_2 to produce electrons. Therefore, all the electrons necessary for the conversion should come from CO. This affects the overall process efficiency since CO is used in electron production rather than in product formation (Ahmed and Lewis, 2007).

4. Microbiology of syngas fermentation

Currently known microorganisms capable of fermenting syngas into ethanol and other bioproducts are predominantly mesophilic (Table 2). The most favorable operational temperature for mesophilic microorganisms is between 37 and 40 °C where as for thermophilic, the temperature varies between 55 and 80 °C. Some thermophilic microbes however, can operate at a higher temperature than reported above (Henstra et al., 2007). Mesophilic microorganisms, e.g., *Clostridium aceticum*, *Acetobacterium woodii*, *C. carboxidivorans* and *C. ljungdahlii* have been widely studied in syngas fermentation (Younesi et al., 2005). Since, syngas exits the gasifier at a very high temperature, it has to be cooled down before introducing into the fermentor. The excess heat release can be recovered by coupling the process with a heat recovery system.

The most favorable pH range for efficient microbial activity varies between 5.8 and 7.0 depending on the species. For example, the optimal pH was reported around 5.8 to 6.0 for *C. ljungdahlii.* An ethanol concentration as high as 48 g/L was obtained in a continuous-flow system at a low pH of 4.0 to 4.5, coupled with a nutrient-limited environment by *C. ljungdahlii* (Klasson et al., 1993). In a separate study, a mesophilic bacterium, *Clostridium carboxidovorans* (or P7), was used in syngas fermentation in a continuously-operated bubble column reactor at pH of 5.75 (Rajagopalan et al., 2002). The authors claimed that the bacterial strain P7 has a higher ethanol selectivity and yield on CO than *C. ljungdhalii* thereby resulting in a higher ethanol production.

The use of thermophiles in syngas fermentation is in an infant stage. There is some merit of evaluating syngas fermentation at thermophilic conditions as the syngas exits the gasifier at a high temperature between 700 to 800 °C. Thermophilic microbes such as *Carboxydocella sporoproducans*, *Desulfotomaculum carboxydivorans*, *Moorella thermoacetica* and *Moorella thermoautotrophica* were found to grow on CO (Table 2). Until recently, there were no thermophiles capable of converting gaseous substrates such as CO and H_2 into organic compounds.

5. Reactor design for syngas fermentation

Both batch and continuous-flow bioreactors have been examined for syngas fermentation. In batch reactors, the gaseous substrate is introduced into the bioreactor and fermented in a closed system. The gaseous substrate is supplied continuously. The liquid samples are withdrawn at a selected time during fermentation. Vega et al. (1990) examined the kinetic parameters through a series of batch experiments. Traditionally, a continuous stirred-tank reactor (CSTR) was examined in syngas fermentation. Bubble column reactors, monolithic biofilm reactors, trickling bed reactors and microbubble dispersion stirred-tank reactors are some of the other common bioreactors which have been studied under both continuous- and batch-mode operations. Different types of reactor configurations employed in syngas fermentation are briefly discussed here.

5.1. Continuous stirred-tank reactor (CSTR)

The continuous stirred-tank reactor is the most common bioreactor employed in syngas fermentation. In CSTRs, gaseous substrate is injected continuously, and a liquid nutrient flow (culture media) is fed into the bioreactor to supplement nutrients for microbial metabolism (Klasson et al., 1992; Vega et al., 1990). The fermentation product is drawn from the system at the same flow rate as the feed. A higher level of agitation or mixing is main-

Table 2
Frequently used mesophilic and thermophilic microorganisms, and their optimum growth conditions.

Species	T_{opt} (°C)	pH_{opt}	Products	References
Mesophilic microorganisms				
Acetobacterium woodii	30	6.8	Acetate	Genthner and Bryant (1987)
Butyribacterium methylotropphicum	37	6.0	Acetate, ethanol, butyrate, butanol	Grethlein et al. (1991), Lynd et al. (1982), Shen et al. (1999)
Butyribbacterium methylotrophicum	37	5.8–6.0	Acetate, Butyrate, Lactate, Pyruvate	Shen et al. (1999)
Clostridium aceticum	30	8.5	Acetate	Sim et al. (2007)
Clostridium autoethanogenum	37	5.8–6.0	Acetate, ethanol	Abrini et al. (1994)
Clostridium carboxidivorans	38	6.2	Acetate, ethanol, butyrate, butanol	Liou et al. (2005)
Clostridium leatocellum SG6	35	7–7.2	Acetate, lactate, ethanol	Ravinder et al. (2001)
Clostridium ljungdahlii	37	6.0	Acetate, ethanol	Tanner et al. (1993)
Eubacterium limosum	38–39	7.0–7.2	Acetate	Genthner and Bryant (1987), Genthner and Bryant (1982)
Mesophilic bacterium P7	37	5.7–5.8	Acetate, ethanol, butyrate, butanol	Rajagopalan et al. (2002)
Oxabactor pfennigii	36–38	7.3	Acetate, n-butyrate	Krumholz and Bryant (1985)
Peptostreptococcus productus	37	7.0	Acetate	Lorowitz and Bryant (1984)
Thermophilic microorganisms				
Carboxydocella sporoproducens	60	6.8	H_2	Slepova et al. (2006)
Clostridium thermocellum	60	7.5–6.0	Acetate	Florenzano and Poulain (1984)
Desulfotomaculum thermobenzoicum subsp. Thermosyntrophicum	55	7.0	Acetate, H_2S	Parshina et al. (2005)
Moorella thermoacetica (Clostridium thermoaceticum)	55	6.5–6.8	Acetate	Daniel et al. (1990)
Moorella thermoautotrophica	58	6.1	Acetate	Savage et al., 1987

tained in the reactor by baffled impellers to enhance the mass transfer between the substrate and the microbes. Higher rotational speeds of the impellers tend to break the gas bubbles into finer ones thereby making the gaseous substrate more accessible to the microbes. In addition, the slow rising velocity of the finer bubbles leads to longer gas retention in the aqueous medium, which leads to higher mass transfer rates.

5.2. Bubble column reactors

Bubble column reactors are designed mainly for industrial applications with large working volumes. Higher mass transfer rates and low operational and maintenance costs are the primary merits of this system, while back-mixing and coalescence are considered to be the major drawbacks of bubble columns (Datar et al., 2004).

5.3. Monolithic biofilm reactors

In monolithic biofilm reactors, the gaseous substrate is allowed to pass through a bed of carrier media. The microbes grow on the media as biofilm. During the operation, attached microorganisms in the biofilm utilize the gaseous substrates to produce ethanol, acetic acid and other end products. The monolithic biofilm reactors are operated under atmospheric pressures, making the process more economically viable.

5.4. Trickle-bed reactor

A trickle-bed reactor is a packed bed, continuous reactor in which the liquid culture flows down through packing media. The syngas is allowed to move either downward (co-current) or upward (counter-current) direction. Since these types of reactors do not require mechanical agitation, the power consumption of trickle-bed reactors is lower than the CSTR (Bredwell et al., 1999).

5.5. Microbubble dispersion stirred-tank reactor

A microbubble dispersion stirred-tank reactor is a stirred-tank equipped with a microbubble sparger. Bredwell et al. (1999) found that the mass transfer of the system increased in two ways. Firstly, decreasing bubble sizes cause internal pressure increases, leading to an increase in the driving force. Secondly, the steady state liquid phase concentration gradient at the surface of the bubble is inversely proportional to the diameter. In other words, the flux increases as the diameter of the bubble decreases.

5.6. Membrane-based system

Composite hollow fiber membranes (HFM) can be used effectively to facilitate the mass transfer in aqueous culture media. Even though, this technique has not been adopted exclusively in syngas fermentation, it was examined for hydrogen and oxygen transfer in water treatment applications (Lee and Rittmann, 2001; Nerenberg and Rittmann, 2004). In the HFM, syngas is diffused through the walls of membranes without forming bubbles. The microbial community grown as a biofilm on the outer wall of the membranes continuously ferment H_2 and CO to ethanol and acetic acid. This innovative approach offers significant advantages in achieving a higher yield and reaction rate, and a higher tolerance to toxic compounds present in syngas (tar, acetylene, NO_x, O_2).

Moreover, these HFM bioreactors can be operated under high pressure with higher mass transfer rates and reduced reactor volumes. Microorganisms which can tolerate high pressures can be utilized in the fermentation process as microbial catalysts (Madigan et al., 1997).

6. Factors affecting syngas fermentations

Syngas fermentation is a microbial-mediated process, which is affected by several factors as discussed in the following section.

6.1. Inhibitory compounds

Biomass-derived syngas often contains additional constituents such as ethylene (C_2H_4), ethane (C_2H_6), acetylene (C_2H_2), tar, ash, char particles and gases containing sulfur and nitrogen (Ahmed et al., 2006; Bridgwater, 1994; Haryanto et al., 2009). These impurities in the syngas affect the efficiency of the fermentation process by potential scaling in pathways, and inhibiting the microbial catalysts resulting in low cell growth and product yield. A study reported cell dormancy, hydrogen uptake shutdowns and a shift in pathways from acidogenesis to solventogenesis and vice versa, when the syngas was used without conditioning (Datar et al., 2004). Ahmed and Lewis (2007) was able to overcome cell dormancy by introducing a 0.025 μm filter to remove tar, ash and other particulate matter from the biomass-derived producer gas. Nitrous oxide (NO) was found to be a potential inhibitor of hydrogenase enzyme activity, which reduced the available carbon for product formation (Ahmed and Lewis, 2007). The inhibitory effects of NO on syngas fermentation can be eliminated by improving the gasification efficiency or by scavenging it using agents such as, sodium hydroxide, potassium permanganate or sodium hypochlorite (Brogren et al., 1997; Chu et al., 2001).

Klasson et al. (1993) studied the sulfur gas tolerance of *C. ljungdahlii*. The authors found that the growth of *C. ljungdahlii* was not significantly affected by H_2S concentrations as high as 5.2% (v/v).

Turn et al. (2003) examined the feasibility of improving fuel characteristics of sugarcane bagasse by introducing pre-treatment methods such as milling and leaching. After an initial milling pre-treatment, the N, S and Cl contents of the sugarcane bagasse were reduced to 0.42, 0.14 and 0.25 (percentage dry-basis) from their initial values of 0.48, 0.22 and 0.65, respectively. Further, the combined pre-treatment of milling-leaching-milling reduced the N, S and Cl contents to 0.35, 0.04 and 0.04, respectively, from their initial values. Such pre-treatments could reduce the production of SO_x and NO_x during biomass gasification.

6.2. Mass transfer

Gas–liquid mass transfer is a rate-limiting step in syngas fermentation process (Klasson et al., 1993; Worden et al., 1991). Mass transfer limitations are inevitable at several points of the diffusion process including the transport of gaseous substrate into gas–liquid interface, its transport into culture media (aqueous phase), the transport of the mixed gases into the stagnant liquid layer around the microbes, and the diffusion of the transported gaseous substrate into the microbial cell. The gas–liquid interface mass transfer is the major resistance for gaseous substrate diffusion.

Diffusion limitations of a gaseous substrate into the culture media results in low substrate uptake by microbes and thus, leads to low productivity. Therefore, knowledge of mass transfer coefficients would be more advantageous to understand the rate of mass transfer. The mass transfer coefficient (k_L) (m/s) for a slightly soluble gaseous substrate can be determined using Eq. (5) (Klasson et al., 1992).

$$\frac{1}{V_L}\frac{dN_S^G}{dt} = \frac{k_L a}{H}(P_S^G - P_S^L) \tag{5}$$

where; N_S^G (mol) is the molar substrate transferred from the gas phase, V_L (L) is the volume of the reactor, P_S^G and P_S^L (atm) are the partial pressures of the gaseous substrate in gas and the liquid

phase, respectively, H (L·atm/mol) is the Henry's law constant and a (m^2/L) is the gas–liquid interface surface area for unit volume.

The difference in the partial pressures of the gaseous substrate $P_S^G - P_S^L$ is the driving force for mass transfer and thus controls the solubility of the substrate. High pressure operation improves the solubility of the gas in aqueous phase. However, at higher concentrations of gaseous substrates, especially CO, anaerobic microorganisms are inhibited. Therefore, the determination of a correlation between the substrate diffusion and the specific substrate uptake rate (q_s) (1/h) is important in order to evaluate the process kinetics (Eq. (6)).

$$q_s = \frac{q_m P_S^L}{K'_p + P_S^L + (P_S^L)^2/W'} \quad (6)$$

where q_m (1/h), W' (atm) and K'_p (atm) are empirical constants. Furthermore, Q_S (mg/L·h), the substrate uptake rate, can be written as $Q_S = q_s X$; where X (mg/L) is the microbial cell concentration. By analyzing the above equation, it can be concluded that the operating pressure of the reactor is inversely proportional to the cell concentration (Vega et al., 1990).

Many earlier studies examined mass transfer using different bioreactor configurations (Bouaifi et al., 2001; Bredwell et al., 1999). Table 3 summarizes the volumetric mass transfer coefficients (k_La) for different reactor configurations under various hydrodynamic conditions.

The most common approach for improving the mass transfer in CSTRs is to increase the agitation speed of the impeller (Bredwell et al., 1999). By implementing this strategy, it is possible to obtain smaller bubbles sizes, thus increasing the gas–liquid interfacial area for efficient mass transfer. However, the high energy requirement of the system greatly reduced its economic viability in industrial-scale syngas fermentations. Consequently, other reactor configurations such as trickling bed reactors, air-lift reactors (Bredwell et al., 1999) and bubble column reactors (Bouaifi et al., 2001; Datar et al., 2004) have been examined for an efficient mass transfer. Bouaifi et al. (2001) compared the mass transfer rates between stirred-tank and bubble column reactors and found that the k_La obtained for the bubble column reactor was higher than that of the stirred-tank reactor. This was mainly due to higher interfacial area obtained in the bubble column. In a separate study, Bredwell and Worden (1998) examined the hydrodynamic and mass transfer properties of microbubble dispersions in a bubble column reactor. The authors concluded that the axial mixing of the microbubble dispersion was considerably less than that of the conventional bubble column reactors.

6.3. Reactor type

Reactor configuration is closely related to the gas–liquid mass transfer efficiency. Thus, reactor design plays an important role in syngas fermentation. High mass transfer rates, low operation and maintenance costs and easy scale-up are some of the key parameters for designing an efficient bioreactor system. Similarly, the bioreactor size greatly depends on the rate of mass transfer for sparingly soluble gases (Vega et al., 1990).

CSTRs are the most commonly used bioreactors for syngas fermentation. Bubble columns, packed bubble columns, trickle-bed reactors and microbubble sparged reactors are some of the other configurations which have been examined for syngas fermentation. Table 4 summarizes some of the performance parameters for various bioreactor configurations.

6.4. Temperature

Temperature effects are important for two reasons. Firstly, it affects the microbial growth and substrate utilization in syngas fermentation and secondly, it affects the solubility of gaseous substrate in aqueous medium. The most favorable growth temperature range for mesophilic microorganisms is from 37 to 40 °C, while for thermophilics, it ranges between 55 and 80 °C. Although, thermophilic operations result in reduction of gas solubility in the culture medium, it increases the rate of mass transfer due to low viscosity.

6.5. pH

pH is an important parameter for the optimal activity of microbial catalysts. The optimum pH for syngas-fermenting microbes varies between 5.5 and 7.5 depending on the species. For example, *C. ljungdahlii* has an optimum pH of 5.8–6.0. The optimum growth

Table 3
Volumetric mass transfer coefficients in various reactor configurations and hydrodynamic conditions.

Reactor configuration	N/(rpm)	Microorganism	Gas	k_La/(h^{-1})	References
Trickle bed	n/a	n/a	Syngas	22.0	Cowger et al. (1992)
Continuous-stirred tank	n/a	n/a	Syngas	38.0	Cowger et al. (1992)
Continuous-stirred tank	200	*B. methylotrophicum*	CO	14.2	Bredwell et al. (1999)
Continuous-stirred tank	300	SRB mixed culture	Syngas	31.0 for CO, 75 for H_2	Bredwell et al. (1999)
Continuous-stirred tank	300	*C. ljungdahlii*	Syngas	35.0 for CO	Bredwell et al. (1999)
Continuous-stirred tank	300	*R. rubrum*	Syngas	28.1 for CO	Bredwell et al. (1999)
Continuous-stirred tank	450	*R. rubrum*	Syngas	101.0 for CO	Bredwell et al. (1999)
Stirred tank - microbubble sparger	200	*B. methylotrophicum*	CO	90.6	Bredwell et al. (1999)
Stirred tank - microbubble sparger	300	SRB mixed culture	Syngas	104.0 for CO, 190.0 for H_2	Bredwell et al. (1999)
Packed bubble column	n/a	*R. rubrum*	Syngas	2.1	Bredwell et al. (1999)
Trickle bed	n/a	*R. rubrum*	Syngas	55.5	Bredwell et al. (1999)
Trickle bed	n/a	SRB mixed culture	Syngas	121.0 for CO, 335.0 for H_2	Bredwell et al. (1999)
Trickle bed	n/a	*C. ljungdahlii*	Syngas	137.0 for CO	Bredwell et al. (1999)
Batch-stirred tank	n/a	*P. productus*	CO	7.15	Vega et al. (1990)
Stirred tank	300	*C. ljungdahlii*	CO	14.9	Klasson et al. (1993)
Stirred tank	400	*C. ljungdahlii*	CO	21.5	Klasson et al. (1993)
Stirred tank	500	*C. ljungdahlii*	CO	22.8	Klasson et al. (1993)
Stirred tank	600	*C. ljungdahlii*	CO	23.8	Klasson et al. (1993)
Stirred tank	700	*C. ljungdahlii*	CO	35.5	Klasson et al. (1993)
Bubble column	n/a	n/a	CO	72.0	Chang et al. (2001)
Stirred tank	400	n/a	CO	75.6	Riggs and Heindel (2006)
Stirred tank	500	*R. rubrum*	Syngas	71.8	Younesi et al. (2008)

SRB: Sulfate-reducing bacteria, N: Agitation speed.

Table 4
Performance parameters of various bioreactors used in syngas fermentation.

Reactor configuration	$k_l a/(h^{-1})$	Variables	References
Stirred tanks	10–500	Agitation speed, gas flow rate	Charpentier (1981)
Bubble columns	18–860	Gas flow rate, bubble size	Charpentier (1981); Bouaifi et al. (2001); Datar et al. (2004)
Packed bubble columns	18–430	Packing media properties, liquid flow rate, gas flow rate	Charpentier (1981)
Packed columns co-current flow	1.5–3670	Packing media, liquid flow rate, gas flow rate	Charpentier (1981)
Packed columns trickled flow	36–360	Packing media, liquid flow rate, gas flow rate	Charpentier (1981)
Microbubble sparged bubble column reactor	200–1800	Bubble size	Bredwell and Worden (1998)
Internal loop airlift reactor	140–220	Aeration rate, pumped liquid flow rate	Fadavi and Chisti (2005)
Airlift reactor with a net draft tube	18–160	Superficial air velocities, reactor pressure	Wu et al. (1992)

pH for some of the commonly used mesophilic and thermophilic microorganisms are given in Table 2.

6.6. Growth media

Growth media provides the microbes with all essential nutrients including minerals, trace elements, vitamins and reducing agents for their maximal growth. The selection of the growth media depends on the selected species and the targeted end products. For example American Type Culture Collection (ATCC) medium 1754 (PETC medium) is used as the growth medium for *C. ljungdahlii*. *Acetobacterium* medium (ATCC medium1019), *Thermoanaerobacter ethanolicus* medium (ATCC medium1190) are some of the frequently used growth media.

6.7. Types of microbes

The selection of appropriate microbes for efficient syngas fermentation is a challenging task. Strict mesophilic anaerobes such as *C. ljungdahlii*, *C. aceticum, Acetobacterium woodii, C. autoethanogenum,* and *C. carboxydeviron* are frequently being used in syngas fermentation (Klasson et al., 1992; Rajagopalan et al., 2002; Younesi et al., 2005). In addition, the isolation and engineering of new microbial species, which are more productive and robust, need to be developed.

7. Product yields of syngas fermentation

Ethanol is the most desirable product in biomass-derived syngas fermentation. Younesi et al. (2005) examined the ethanol and acetate production during syngas fermentation using *C. ljungdahlii*. Under normal growth conditions, the wild-type strain of *C. ljungdahlii* was found to produce mainly acetic acid with an ethanol-to-acetate ratio of 0.05, and ethanol concentrations of $\leqslant$0.1 g/L (Vega et al., 1990). Several studies focused on improving the ethanol yield in *Clostridia* through the addition of a reducing agent, the supplementation of additional media constituents, pH shifts, the addition of hydrogen, and providing nutrient-limiting conditions. A condition that induces sporulation has also been found to favor solventogenesis (Klasson et al., 1990).

The addition of yeast extract (0.02%) followed by cellobiose, produced a molar ethanol-to-acetate ratio of 1.0, with ethanol concentrations as high as 3.0 g/L (Klasson et al., 1990). The authors further reported an improved molar ethanol-to-acetate ratio (>1.1) with the supplementation of a reducing agent (Benzyl viologen: 30 ppm). Klasson et al. (1993) reported a drastic improvement in the ethanol yield with *C. ljungdahlii* when the pH was dropped to 4.0–4.5 and a nutrient-limited media was used. The corresponding ethanol concentration was as high as 20 g/L with an acetate concentration of only 2–3 g/L in a complete-mix reactor using coal-derived syngas (H_2: 25–35%, CO: 40–65%, CO_2: 1–20%, and CH_4: 0–7%). The authors reported a maximum ethanol concentration of 48 g/L using this microbe during 560 h of operation. The corresponding acetate concentration was around 3 g/L. Maximum product and cell yields obtained from different studies are summarized in Table 5.

8. Integrated biorefinery

An integrated biorefinery is a facility which is capable of converting lignocellulosic feedstocks into a range of biofuels, chemicals and other bio-based products (Chum and Overend, 2001). Biorefineries utilize the resources more sustainably without producing wastes and other environmental pollutants.

Ethanol is one of the most desirable products of a biorefinery and is mainly used as a transportation fuel after blending with gasoline. Ethanol has an energy content of about two-third that of gasoline. Ethanol blend with gasoline up to 10% can be used in regular gasoline engines without additional modifications (Brown, 2003). Acetic and butyric acids, and butanol are some of the important byproducts in addition to ethanol from biomass-derived syngas fermentation (Datar et al., 2004). Nanoparticles such as mesoporous silica (MPS) functionalized with an amine group has a significantly higher surface area-to-mass ratio and can selectively adsorb acetic acid from the fermentation broth. The adsorbed acid can be recovered readily as a high-value byproduct. The acetic acid can provide an additional revenue stream as it is a starting material

Table 5
Maximum product and cell yields from different studies.

Microorganism	Ethanol/(g/L)	Acetate/(g/L)	Cell yield/(g cell/g)	References
C. ljungdahlii	48.0	3.0	0.45	Klasson et al. (1993)
C. ljungdahlii	3.0	2.0–3.0	–	Klasson et al. (1990)
C. ljungdahlii	0.062*	0.094*	1.378**	Phillips et al. (1994)
Bacterium P7	0.15*	0.025*	0.25**	Rajagopalan et al. (2002)
C. ljungdahlii	0.55	1.3	0.3	Younesi et al. (2005)
C. ljungdahlii	11.0–12.0	28.0	1.15	Najafpour and Younesi (2006)

Note: Units: * - mol C in products per mol CO consumed; ** - g/mol of CO.

for the synthesis of various polymers such as vinyl acetate and acetic anhydride which traditionally use petroleum-based feedstocks (Khanal, 2008; Yoneda et al., 2001). The MPS nano-materials can then be regenerated through pH control. The acetic acid-free broth is perpetually recycled back to the fermenter to supplement the needed nutrients. Butyric acid has potential applications as a flavoring agent in the food processing industry (Zigova et al., 1999). Butanol is used as a raw material for butyl acetate and butyl acrylate production, which can be used as fuel additives to enhance the octane rating of gasoline (Grethlein and Jain, 1992).

The lignin component of the lignocellulosic biomass is considered as a low-value residue in conventional biochemical-based ethanol plants. Therefore, for the biorefinery concept to be applicable for a wide range of lignocellulosic feedstocks, lignin should be integrated into the process effectively (Chakar and Ragauskas, 2004).

Regardless of the technology used in a biorefinery, the processes will generate some percentage of waste products that will be difficult to convert further into value-added products. These waste products generally contain lignin, carbohydrate residues and other organic compounds. Such waste products and other lignin residues can be easily integrated into the biorefinery by thermochemical pathways, by producing syngas (Sricharoenchaikul et al., 2002). The produced syngas can be converted into ethanol by using either microbial fermentation or FT synthesis.

9. Economics and scale-up feasibilities of syngas fermentation

A techno-economical analysis plays an important role to guide investors and policy makers to select the most effective technology. Piccolo and Bezzo (2009) compared the techno-economical factors of bioethanol production by two pathways, namely enzymatic hydrolysis and fermentation (a biochemical pathway) and the gasification followed by syngas fermentation (a thermochemical pathway). The comparison was carried out by considering some important factors including modeling, process optimization, heat and power generation, process sensitivity and financial analysis. The authors calculated the production cost of ethanol per gallon for the two processes, and the biochemical pathway was found to be more economically feasible than the thermochemical pathway. A summary of the results of that study is shown in Table 6.

Wei et al. (2009) conducted an overall process evaluation of ethanol production from wood by three pathways, namely acid hydrolysis followed by fermentation, gasification biosynthesis (syngas fermentation by a biocatalyst) and gasification chemical synthesis (FT synthesis). The authors compared the three pathways according to the mass and energy balances. The study revealed that the FT synthesis showed the highest processing rate (1 day) and the lowest water consumption. On the other hand, hydrolysis fermentation had the highest energy and water consumption and a modest processing rate (5 days). The authors further reported that syngas fermentation by biocatalysts had the highest mass and energy conversion rate with the lowest processing rate (28 days).

Since the published research data on the techno-economic analysis of microbial syngas fermentation is very limited, it is difficult to draw a firm conclusion on economic feasibility of this process. Coskota is leading an effort towards commercialization of syngas fermentation technology. The details can be found in </http://www.coskata.com/>.

Table 6
Comparison of the selling price of ethanol based on the feedstock cost and the effect of yield in enzymatic hydrolysis and gasification fermentation processes.

		Enzymatic hydrolysis and fermentation/ ($/L ethanol)	Gasification and fermentation (microbial)/ ($/L ethanol)
Feedstock cost/($/dry ton of biomass)	63	1.16	1.79
	54	1.12	1.68
	45	1.08	1.67
	36	1.04	1.60
Effect of fermentation yield	Base case	1.12	1.68
	Mid-term	0.95	1.51
	Long-term	0.84	1.32

Note: all the calculations are for a 5 year payback period.
Source: modified from Piccolo and Bezzo, 2009.

10. Key performance index

Biomass pre-treatment, feedstock properties, gasification method, gas clean-up and conditioning, and fuel synthesis are among the key performance parameters associated with syngas fermentation (McKendry, 2002). Biomass pre-treatment can be further subcategorized into unit processes such as drying, size reduction, fractionation and leaching. In general, before gasification the moisture content of the biomass should be lowered to less than 15% and the typical feed particle size is around 20–80 mm. Fractionation and leaching with water aim at reducing the nitrogen and alkali content of the feedstocks to produce high purity gas mixture.

Characteristics of the biomass feedstocks such as moisture and ash contents, and volatile compounds have a significant impact on syngas fermentation. Biomass with moisture contents above 30% makes the gasification not only difficult but also reduces the calorific value of the produced gas (McKendry, 2002). Higher mineral content of the biomass leads to a higher ash production during gasification. Clinkering or slagging problems in the pipe lines are common in biomass with higher ash contents. Production of tar and other volatile substances during gasification leads to cell dormancy and process inhibitions in syngas fermentation (Ahmed and Lewis, 2007).

Gasification technology is a key operational parameter in syngas fermentation. In general, there are two major types of gasifiers namely, fixed bed and fluidized bed gasifiers. Fixed bed gasifiers are further classified as updraft, downdraft or cross-flow depending on the airflow direction. Generally, fixed bed gasifiers produce lesser amount of particulate matter than fluidized bed gasifiers, where as the calorific value of the produced gases in the fixed bed gasifier is lower than that of the fluidized bed gasifiers. However, fixed bed gasifiers are relatively simple in design compared to the complex design of the fluidized bed.

Gas clean-up and conditioning remove the problematic tars, chars, particulate matters and other contaminants which cause pipe slaggings and downstream process inhibitions. Cyclones, adsorption columns, water or oil scrubbers and various types of filters are some of the common syngas purification unit operations.

Fuel synthesis and the product recovery are the key parameters that describe the efficiency and the economic feasibility of the fermentation process. Further, the efficiency of the process can be increased by adapting innovative reactor designs with higher mass transfer rates, new biocatalysts with increased product yields and efficient product recovery methods such as membrane separation and the use of nanotechnology. It is important to point-out that biomass-derived syngas fermentation to biofuel is still at infant stage of development. Many of these indices are yet to be identified and quantified based on pilot and full-scale biorefineries.

11. Challenges and future research directions of syngas fermentation

11.1. Mass transfer limitation

Gas-to-liquid mass transfer limitation is still considered as one of the major challenges for the commercialization of syngas fermenta-

tion technology. Volumetric mass transfer coefficient (k_La, which is a direct measurement of the hydrodynamic condition of a reactor) can be used as a reliable parameter to compare the mass transfer capabilities in various reactor configurations. Advancements in impeller designs, fluid flow patterns, aerated power efficiency, mixing time, baffle design and the use of microbubble dispersers are some of the conventional approaches examined in literature to improve the mass transfer limitations. The use of HFM in syngas fermentation is an innovative approach which offers significant advantages over the conventional reactor configurations.

11.2. Quality of syngas

Syngas should be free from impurities such as tars, ash, ethylene, ethane, acetylene and gases containing sulfur (SO_x) and nitrogen (NO_x) before being introduced into the fermentation process. Several gas clean-up approaches are currently available for syngas fermentation including mechanical methods such as cyclones, various types of filters (fabric, ceramic and bag filters), rotating particle separators, water scrubbers and wet electrostatic precipitators (Hasler and Nussbaumer, 1999). In addition, by implementing appropriate gasification and preprocessing techniques (such as milling and leaching), the production of impurities (S, N and Cl compounds) can be reduced considerably at the source. This technique has been successfully examined for sugarcane family feedstocks (such as sweet sorghum, banagrass, miscanthus) to reduce nitrogen and sulfur containing compounds (Turn et al., 2003).

11.3. Microbial catalysts

The isolation of anaerobic microorganisms capable of converting syngas into ethanol and other bioproducts with higher product yields is another important aspect of commercialization of the process. In this case, thermophilic microorganisms which can convert CO into higher value organic compounds such as ethanol or butanol might be an interesting area to study. On the other hand, the genetic modification of existing syngas-fermenting microbes to create "high yield anaerobes" is another important challenge.

11.4. Product recovery

Although distillation is being used as the traditional method of separating ethanol from a mixture of water and other syngas fermentation byproducts, high energy costs challenge the continuation of this method. Ultrasonic atomization, vapor recompression, vapor reuse and vacuum distillation, and selective adsorption of water are some of the alternative methods that have been examined in order to reduce the ethanol recovery cost (Sato et al., 2001).

Liquid–liquid extraction is a widely used separation technique for acetic acid recovery. A suitable solvent can be used in order to extract a substantially pure acetic acid solution. Fockedey et al. (2008) proposed a novel extraction/re-extraction method using glycerol as one of the solvents to recover ethanol, acetic acid and other byproducts.

11.5. Redirection of metabolic pathway

Syngas fermentation is always associated with acid production, which lowers the culture pH. Low pH provides an unfavorable environment for solvent production by clostridia. Redirecting the metabolic pathway towards solvent production by blocking acid production might enhance ethanol production. More research is needed in this area.

11.6. Technology road map

According to the recommendations by the technical advisory committee to the US Department of Agriculture and the US Department of Energy, following research areas are identified as strategically significant to increase the biofuel production in the future: (a) feedstock development, (b) conversion processes, (c) systems integration, and (d) marketing and public policy issues (The Northeast Sun Grant Northeast Region, 2004).

Technological advances in feedstock development reduce the production cost of biofuel. This includes the improvements in existing biomass resources in terms of yield, sustainability and development of new non-food plant strains capable of growing under extreme environmental conditions with higher energy density.

Advanced biomass processing and conversion technologies increase the overall efficiency of the process, while lowering the negative environmental impacts. Refining and developing advanced separations methods, optimization of microbial fermentations, developing small-scale conversion systems are among some of the significant future research areas under the processing and conversion technologies.

System integration involves the development of efficient harvesting, storage and transportation systems and synergetic effect of biorefineries to optimize economic, social and environmental benefits.

Marketing and public policy issues including incentive schemes for biofuel industry, efficient land use for feedstocks and increased public awareness towards sustainable bio-based economy play an important role in future biofuel industries.

12. Conclusions

Biofuel production from lignocellulosic biomass feedstocks is identified as a sustainable alternative for growing energy demands and has several advantages such as a higher availability of biomass, no competition with food and low feedstock cost. Gasification of lignocellulosic biomass produces synthesis gas which predominantly consists of H_2 and CO. Microbial syngas fermentation into biofuel has significant advantages over the metal catalytic (FT synthesis) conversions. Gas–liquid mass transfer limitations, syngas quality, microbial catalysts and product recovery are the major issues to be addressed in order to make syngas fermentation more economically feasible. Reactor designs which are closely related with mass transfer properties are being discussed extensively in recent studies. The use of HFM in syngas fermentation is an innovative approach which can offer significant contributions to improve mass transfer compared to conventional reactor designs.

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