



PROBLEMS

Problem 1

A certain crop has photosynthetic efficiency equal to 0.5% and power conversion efficiency of 32%. The crop is subjected to insolation at 850 kWh/m². Estimate the land area required to generate 0.5 GW of electricity steadily over a year.

- (A) 3.22 km²
- (B) 32.2 km²
- (C) 322 km²
- (D) 3220 km²

Problem 2

The general chemical formula for a biomass fuel is CH_{1.5}O_{0.67}. What is the mass of air required for the complete combustion of 1 kg of this biomass with 30% excess air?

- (A) 5.93 kg
- (B) 7.71 kg
- (C) 9.44 kg
- (D) 9.82 kg

Problem 3

Regarding research on biomass energy, are the following statements true or false?

1. () The contents of ash-forming elements in biomass fuels vary greatly, but accurate knowledge of chemical composition is crucial for prospective applications such as soil fertilization. In one important contribution, Zajac *et al.* (2018) studied the composition of ashes from 35 biomass species including woody biomass, agricultural biomass, and agri-food industry wastes. Those workers noted that the ash samples obtained from most species had relatively low contents of calcium, potassium, phosphorus, and sulfur; since these are plant micronutrients, Zajac's group ruled out use of most biomass types as agricultural fertilizers.

Recommended research: Zajac *et al.* (2018).

2. () Torrefaction may be viewed as a mild or incomplete form of slow pyrolysis. Benefits of torrefied biomass and char as solid energy carriers include increased energy density, hydrophobicity, and grindability. Moreover, properly torrefied biomass can be made carbon-rich and can be used as a substitute of coal in coal-based applications including use as a gasifier feed or as a reducing agent in metallurgical smelting processes.

Several processes have been proposed to produce liquid fuels from lignocellulosic biomass, and fast pyrolysis is one of the most promising ones. Fast pyrolysis is the rapid thermal degradation of organic materials in the absence of oxygen, at rates in the range of 500°C/s, to a final temperature of 500 – 600°C. The rapid heating decomposes large molecules of biomass into smaller ones, which are released in the form of volatile compounds. The volatiles are then quickly cooled back to room temperature, generating a brownish liquid fuel usually referred to as ‘bio-oil.’

3.() Bio-oil can be used for applications such as heating, electricity generation, and production of commercially relevant chemicals. Its main application, however, is as a transportation fuel, for which bio-oil serves nicely due to its low oxygen content, miscibility with conventional hydrocarbon fuels, and low acidity. ■ (A black square indicates the end of a multi-paragraph statement.)

Recommended research: Resende (2016).

Thermochemical gasification of biomass with high moisture content is considered uneconomical because it calls for a drying pretreatment that may involve an energy load comparable to the energy content afforded by the biomass itself. In view of this limitation, supercritical water gasification has emerged as an alternative to conventional gasification of wet biomass, as it does not require drying and takes place in shorter residence times.

4.() D’Jesús *et al.* (2006) carried out gasification of corn starch, clover grass and corn silage in supercritical water, aiming to study the effects of process conditions such as temperature and residence time. D’Jesús’ group also attempted to evaluate the effect of inclusion of potassium, deployed as KHCO_3 , in the three biomass products. Addition of KHCO_3 was found to increase the gasification yield of all three products. ■

Recommended research: D’Jesús *et al.* (2006).

Hydrogen gas is regarded as a sustainable fuel because its combustion releases no greenhouse gases. However, at present most industrial hydrogen comes from steam reforming of natural gas, which, needless to say, is not at all a sustainable process. There is now a growing interest in alternative schemes for production of this important fuel.

Waheed and Williams (2013) studied the production of H_2 via pyrolysis-steam reforming and pyrolysis-catalytic steam reforming of rice husk, sugar cane bagasse, and wheat straw in a two-stage reactor system. Calcined dolomite and 10 wt% Ni-dolomite were used in the second stage to enhance hydrogen production. Waheed and his colleague intended to compare the hydrogen production from the three different biomass samples.

5.() Of the three biomass samples investigated, the greatest hydrogen yield was obtained from the pyrolysis/reforming of sugar cane bagasse catalyzed by 10 wt% Ni-dolomite. ■

Recommended research: Waheed and Williams (2013).

At present, industrial hydrogen production methods include water electrolysis, methanol steam reforming, and steam catalytic conversion of heavy oil and natural gas. Water electrolysis consumes massive amounts of electricity, which leads to high product cost. Methanol steam reforming, while economical, uses non-renewable fossil fuels and generates CO_2 as a byproduct. Steam catalytic conversion of heavy oil and natural gas is likewise not sustainable.



In comparison, hydrogen production from biomass is an efficient, energy-saving, and environmentally friendly alternative. Steam gasification and supercritical water gasification are two extensively researched routes for industrial production of H_2 via biomass. As noted in an extensive review by Cao *et al.* (2020), both of these processes can benefit from use of certain catalysts, which decrease reaction temperature, improve carbon gasification rate, and increase hydrogen selectivity from biomass.

6.() Nickel-based catalysts, commonly used in steam gasification, may greatly enhance the hydrogen yield of supercritical water gasification. What’s more, nickel-based catalysts in SCWG are not deactivated by tar-forming products. ■

Recommended research: Cao *et al.* (2020); Okolie *et al.* (2019).

7.() Ozbas *et al.* (2019) reported an interesting application of supervised machine learning to hydrogen production via biomass. A laboratory-scale updraft gasifier was used to process olive pit waste and gather data. Then, an assortment of four machine learning techniques – linear regression, k nearest neighbors regression, support vector machine regression, and decision tree regression – was implemented to predict the volume percentage of H₂ generated on the basis of inputs including time, temperature, concentrations of reactants, and heating value. Ozbas’s group noted that all four models performed very well in predicting the hydrogen concentration associated with the process; specifically, all four models had R^2 coefficients greater than 0.90.



Recommended research: Ozbas *et al.* (2019).

8.() Particular attention is paid to the condensable phase of biomass gasification products. This type of product, known as *tar*, has a rather complex chemical composition and is conveniently divided into three categories – primary, secondary, and tertiary – according to its position in the biomass decomposition process. Importantly, tertiary tars and primary tars do not coexist in the same gasified biomass sample.

Recommended research: Milne *et al.* (1998).

9.() Indeed, formation of tar may be the most important impediment to the practical implementation of biomass and organic waste gasification. It is worth noting that tar modelling has kept researchers occupied for several years; in a meta-analysis of 54 model-driven studies of biomass gasification published between 2000 and 2017, Safarian *et al.* (2019) noted that more than half involved models that accounted for tar formation and development.

Recommended research: Safarian *et al.* (2019).

Catalytic treatment is considered one of the best options for elimination of tar from syngas. Catalysts tentatively employed for this purpose include dolomite, olivine, nickel, and alumina. Dolomite is considered particularly promising because of its low cost and positive additional effects such as a reported increase in the heating value of syngas.

10.() Pinto *et al.* (2015) investigated the effect of several parameters on the performance of laboratory-scale gasification of lignin pellets. One of the modifications Pinto’s group experimented with was the inclusion of one of three mineral catalysts, namely lime, olivine, and dolomite. Of these three materials, the greatest reduction in tar content occurred when gasification was catalyzed by dolomite. ■

Recommended research: Pinto *et al.* (2015).

Several techniques for removal of tar from biomass gasification products have been researched in recent years. Two particularly promising methods are catalytic reforming and plasma reforming, but both have important shortcomings. One recently proposed solution would be to integrate both techniques in a single tar reforming scheme, known as *hybrid plasma-catalysis system* (HCPS), so that the individual disadvantages of each method can be overcome and a synergistic effect can be achieved. HCPS has been reviewed by Liu *et al.* (2019).

11.() An HCPS formulation is prepared by combining a heterogeneous catalyst with either a thermal plasma or a non-thermal plasma. ■

Recommended research: Liu *et al.* (2019).

Hydrothermal carbonization is similar to torrefaction – so much so, in fact, that some refer to it as ‘wet torrefaction.’ However, it possesses some advantages over torrefaction, most notably the fact that, being conducted in an aqueous environment, HTC can easily utilize water-rich feedstocks such as municipal waste streams, peat, and algae.

12.() Yet another advantage of hydrothermal carbonization over torrefaction, discussed in Reza *et al.* (2012), is that HTC hydrochar is more amenable to pelletization than is char from torrefaction – a crucial advantage for commercial development of solid biofuels. ■

Recommended research: Hoekman *et al.* (2013); Reza *et al.* (2012).

Hydrothermal carbonization (HTC) has emerged as a potential alternative to conventional waste-to-energy techniques such as anaerobic digestion. HTC allows for smaller required treatment footprints, more efficient conversion of mixed wastes, and greater waste volume reductions. What's more, carbonization results in the production of an easily stored energy-rich resource.

13.() Li *et al.* (2013) evaluated the carbonization of food waste and typical food packaging materials to establish how process conditions such as feedstock composition and reaction temperature affect the properties of the treated product. Of note, Li's group found that inclusion of packaging materials in the fuel blend to be carbonized had no statistically significant effect on the energy content of the recovered solids obtained after HTC. In other words, as the proportion of packaging materials was increased, the energy content of the recovered solids remained essentially the same. ■

Recommended research: Li *et al.* (2013).

14.() Hoekman *et al.* (2013) performed hydrothermal carbonization of six lignocellulosic biomass feedstocks – three woody and three herbaceous – and went on to characterize the extent of energy densification of hydrochar that is readily achievable over a practical range of HTC process conditions. Hoekman's group reported that energy density of HTC products increased with temperature, be it for woody or herbaceous feedstock.

Recommended research: Hoekman *et al.* (2013).

Through analytical techniques, Reza *et al.* (2014) tried to elucidate the reaction chemistry of hydrothermal carbonization as applied to loblolly pine. Steps involved in HTC include hydrolysis, dehydration, decarboxylation, aromatization, and polymerization. Reza's group devoted substantial effort to the water balance of HTC, which is uncertain because one of these reactions (namely, hydrolysis) requires water whereas others (namely dehydration, polymerization) produce water.

15.() Reza's group noted that, as hydrolysis and dehydration occur simultaneously, the water balance may reflect competition between these two reactions. Indeed, Reza's group verified that because a net loss of water was observed for all temperatures they tested, it seems likely that hydrolysis is more prominent than dehydration in HTC of loblolly pine. ■

Recommended research: Reza *et al.* (2014).

Thermochemical methods are the current leading pretreatment technologies for lignocellulosic biomass used in bioethanol production. However, these methods have several drawbacks: they require expensive corrosion-resistant reactors, extensive washing of treated solids, and detoxification of compounds inhibitory to ethanol-fermenting microorganisms.



16.() Fungal pretreatment with lignin-degrading microorganisms, usually white rot fungi, has emerged as an alternative approach to thermal-chemical pretreatment for cellulosic ethanol production. Advantages include low energy requirements, reduced downstream processing costs, and reduced inhibitors to ethanol fermentation. The main advantage of fungal degradation of lignocellulosic biomass, however, is the inherently lower pretreatment time when compared to even the most cutting-edge thermochemical processing schemes. ■

Recommended research: Wan and Li (2012).

17.() Dilute acid hydrolysis (DAH) is one of the leading technologies for lignocellulosic pretreatment in bioethanol production. This method is often adopted in large scale applications because of its low cost. As of the early 2020s, the mineral acid most commonly used in industrial DAH pretreatment was perchloric acid, HClO₄.

Recommended research: Loow *et al.* (2016).

18.() Combination of fungal lignocellulosic biomass pretreatment with acid pretreatment has also been attempted. Working with water hyacinth samples, Ma *et al.* (2010) combined a mild acid pretreatment and a pretreatment with white rot fungus to assess whether the co-treated feedstock would yield a greater reducing sugar yield upon enzymatic hydrolysis or a greater ethanol yield upon fermentation by *Saccharomyces cerevisiae*. Results were encouraging in both cases, as the co-treated water hyacinth samples afforded a greater reducing sugar output and a greater ethanol output than those obtained from samples pretreated with acid only.

Recommended research: Ma *et al.* (2010).

Another approach to lignocellulosic biomass pretreatment is alkaline hydrolysis. Alkali pretreatment promotes the removal of lignin, which in turn enhances the reactivity of the remaining polysaccharides. Alkaline agents proposed for this application include sodium hydroxide (NaOH), lime (CaO), and ammonia (NH₃).

19.() The main ammonia-based alkaline pretreatment technology is ammonia fiber explosion (AFEX), whereby lignocellulosic biomass is exposed to liquid NH₃ at high temperature and pressure. AFEX pretreatment is associated with high sugar yields and low inhibitor production for downstream biological processes, so that the biomass washing step after pretreatment can be altogether avoided. ■

Recommended research: Loow *et al.* (2016).

Ionic liquids (ILs) have been considered as promising solvents for pretreatment of lignocellulosic biomass. One particular IL, 1-ethyl-3-methylimidazolium acetate, [C₂C₁im][OAc], has been considered for commercial use and possesses advantages such as acceptable compatibility with existing biorefinery equipment and effectiveness figures that are largely independent of biomass type. Like many other ionic liquids, however, [C₂C₁im][OAc] is relatively expensive, and cost is regarded as the main hurdle for adoption of this type of solvent in industrial pretreatment.

20.() George *et al.* (2015) attempted to synthesize more accessible ionic liquids by using a combination of simple organic amines and sulfuric acid, two cheap, readily available sources of charge-carrying species. Of the ILs prepared by George's group, the best performance came from diisopropylammonium hydrogen sulfate, which, when applied to lignocellulose pretreatment, registered a glucose hydrolysis yield within 75% of treatment using [C₂C₁im][OAc]:H₂O under the same thermochemical conditions. ■

Recommended research: George *et al.* (2015).

21.() Ozonation has also been investigated as a technique for pretreatment of lignocellulosic biomass. In one important contribution, García-Cubero *et al.* (2009) sought to determine the influence of process parameters on the ozonolysis pretreatment of rye and wheat straw, two materials with markedly different proportions of lignin. They used a design-of-experiments framework to study the effect of each process variable, and found that moisture content and biomass type were most important. They also tested the effect of ozonation in a basic medium, hydrating a few samples with 20% NaOH solution before ozonation and introducing pH as a variable in a separate factorial design. García-Cubero's group went on to note that ozonation in a basic medium led to no statistically significant differences in extent of delignification or degradation of cellulose.

Recommended research: García-Cubero *et al.* (2009).

22.() Pretreatment with the organic solvent N-methylmorpholine-N-oxide (NMMO) has been investigated for ethanol production from materials such as sugarcane bagasse and cotton. Teghammar *et al.* (2012) investigated the effects of pretreatment with NMMO on lignocellulosic waste materials for biogas production. Softwood spruce, rice straw, and triticale were pretreated with NMMO before being fed to an anaerobic digester to produce biogas. Teghammar's group noted that, for all three products, the methane yield afforded by the lignocellulose pretreated with NMMO was superior to that of untreated lignocelluloses. On the other hand, recovery of solvent was poor in all three cases, which is a serious practical hurdle because NMMO is an expensive solvent.

Recommended research: Teghammar *et al.* (2012).

Coal and biomass co-conversion has been regarded as a greener alternative to firing of coal on its own. Lifecycle assessments on co-firing of coal and biomass have shown that CO₂ emissions decline proportionally to the amount of coal offset by biomass, considering biomass as a carbon-neutral source produced sustainably.

23.() As noted in an extensive review by Tchapda and Pisupati (2014), thermodynamic equilibrium of co-gasification shows that the amount of gases generated increases as the percentage of biomass in the blend increases, leading to greater gross calorific value and coal gas efficiency of the product gas. ■

Recommended research: Tchapda and Pisupati (2014).

Oladejo *et al.* (2017) investigated the synergistic interaction between coal and biomass using a low rank coal and its blends with different biomass samples at various blending ratios. Oladejo's group introduced a so-called *synergy factor* (SF) to aid designers in the selection of a proper biomass for co-processing with coal and to determine the proper blending ratio to enhance synergistic interaction. The index could also be used to evaluate the different impacts of catalytic effects afforded by minerals from biomass.

24.() In the framework of the synergy factor proposed by Oladejo's group, a fuel blend with SF equal to, say, 1.5 would be associated with a strong synergistic effect. ■

Recommended research: Oladejo *et al.* (2017).

Researchers are now making strides in the many applications associated with biochars (BCs), the products of thermal degradation of biomass. For example, several workers have studied the application of biochars as adsorbents in the removal of heavy metals from wastewater. Arán *et al.* (2016) studied the capacity of biochars of different origin – specifically, BCs obtained from chicken manure, eucalyptus, corn cob, olive mill waste, and rice husk – in the adsorption of copper, all the while aiming to explore the influence of biochar composition in the retention of this metallic pollutant.

25.() Arán's group examined the influence of pH on copper adsorption in two of the biochar samples, namely those obtained from rice husk and chicken manure, and reported that, for both samples, the copper retention capacity increased with the pH of the aqueous medium in which adsorption was carried out. ■

Recommended research: Arán *et al.* (2016).

Problem 4

Calculate the lower and higher heating values of propane (C₃H₈) at standard conditions. The molar enthalpies of formation of CO_{2(g)}, H₂O_(l), and C₃H_{8(g)} are respectively –393.5 kJ/mol, –285.8 kJ/mol, and –104.7 kJ/mol. The latent heat of vaporization of water is 44,000 kJ/kmol.

- (A) LHV = 51,250 kJ/kg; HHV = 59,230 kJ/kg;
- (B) LHV = 51,250 kJ/kg; HHV = 61,450 kJ/kg;
- (C) LHV = 55,230 kJ/kg; HHV = 59,230 kJ/kg;
- (D) LHV = 55,230 kJ/kg; HHV = 61,450 kJ/kg;

Problem 5 (Modified from Turns, 2012)

A droplet of octane, C₈H₁₈, has initial diameter equal to 850 μm and is evaporating in quiescent nitrogen at 500 K. The boiling point of octane is approximately 400 K, its heat of vaporization is 300 kJ/kg, and its density is 703 kg/m³. The thermal conductivities of *n*-octane and molecular nitrogen at 450 K are 0.033 W/m·K and 0.04 W/m·K, respectively, and the specific heat capacity of *n*-octane at this same temperature is 2.51 kJ/kg·K. What is the droplet lifetime?

- (A) 4.8 sec
- (B) 7.7 sec
- (C) 9.2 sec
- (D) 11 sec

Problem 6 (Modified from Wijesundera, 2022)

The following data apply to a corn ethanol plant. Calculate the net energy balance of the ethanol production process.

- Feedstock corn required per liter of ethanol: 2.4 kg
- Corn yield per hectare of land: 9280 kg
- Net energy available in a liter of ethanol: 22 MJ
- Energy required per hectare of land to grow corn:
 - Machinery: 4.6 GJ
 - Fossil energy: 5.9 GJ
 - Nitrogen: 8.2 GJ
 - Additional energy inputs: 4.0 GJ
- Energy inputs to the ethanol production process per 1000 liters of ethanol:
 - Transportation: 1.2 GJ
 - Steam for distillation: 9.2 GJ
 - Electricity: 4.5 GJ
 - Additional energy inputs: 0.4 GJ

(A) $NEB = 1.04$

(B) $NEB = 1.09$

(C) $NEB = 1.14$

(D) $NEB = 1.19$

SOLUTIONS

■ Problem 1

The yearly energy required is

$$E_e = (0.5 \times 10^9) \times 24 \times 365 = 4.38 \times 10^{12} \text{ Wh} = 4.38 \times 10^9 \text{ kWh}$$

In turn, the energy available from biomass is

$$E_{bm} = A \times 850 \times \frac{0.5}{100} \times \frac{30}{100} = 1.36A$$

where A is the cultivated area. Equating E_e and E_{bm} and solving for A , we get

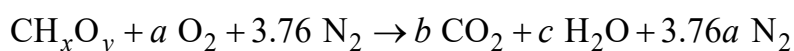
$$E_e = E_{bm} \rightarrow 4.38 \times 10^9 = 1.36A$$
$$\therefore A = \frac{4.38 \times 10^9}{1.36} = 3.22 \times 10^9 \text{ m}^2 = \boxed{3220 \text{ km}^2}$$

This is a large area, equivalent to a square-shaped plantation with side equal to approximately 56.7 km. The large cultivated land area required to achieve a reasonably high power output continues to be one of the main disadvantages of biomass energy.

◆ The correct answer is **D**.

■ Problem 2

The general chemical reaction for stoichiometric combustion of organic matter in air is



We proceed to write mass balance equations. For oxygen,

$$y + 2a = 2b + c$$

For hydrogen,

$$x = 2c$$

For carbon,

$$1 = b$$

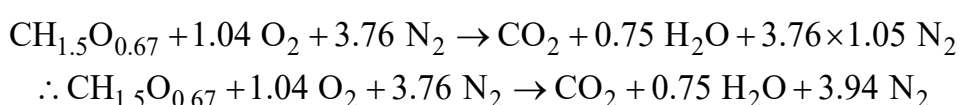
Solving for a brings to

$$a = \frac{1}{2} \left(2 + \frac{x}{2} - y \right) = \frac{1}{2} \left(2 + \frac{1.5}{2} - 0.67 \right) = 1.04$$

Also,

$$c = \frac{x}{2} = \frac{1.5}{2} = 0.75$$

The chemical equation then becomes



From the stoichiometry of the reaction above, the mass of fuel is determined as

$$m_f = 12 + 1.5 \times 1 + 0.67 \times 16 = 24.2 \text{ kg}$$

The mass of oxygen is

$$m_o = 1.04 \times 32 = 33.3 \text{ kg}$$

The mass of air, assuming it is constituted of oxygen and nitrogen only, follows as

$$m_a = 33.3 + 3.94 \times 28 = 143.6 \text{ kg}$$

The mass of air per kg of fuel is then

$$\frac{m_a}{m_f} = \frac{143.6}{24.2} = 5.93$$

or, with 30% excess air,

$$\frac{m_a}{m_f} \times 1.30 = 7.71$$

Thus, the mass of air required for complete combustion of 1 kg of biomass at 30% excess air is 7.71 kg.

◆ The correct answer is **B**.

■ Problem 3

1. False. Zajac *et al.* (2018) actually found that the ash products had appreciable contents of Ca, K, P, and S, which suggests a likely usefulness for agricultural fertilizing purposes. What's more, most ash products, with the exception of wood biomass, exhibited low contents of toxic elements such as arsenic and lead. Zajac's group also noted that ashes obtained from biomass combustion were enriched with micronutrients such as zinc, copper, and manganese.

Reference: Zajac *et al.* (2018).

2. True. Through torrefaction and slow pyrolysis, the composition of the solid product approaches that of coal by becoming relatively more carbon-rich at the expense of oxygen and hydrogen. Torrefied biomass or char could therefore be incorporated within existing coal-based processes – such as a fuel for coal-fired boilers or a feed to gasifiers – with greater ease than unprocessed biomass.

Reference: Nachenius *et al.* (2013).

3. False. As noted by Resende (2016), use of bio-oil as a transportation fuel remains problematic because of its high oxygen content (which leads to a low heating value), its immiscibility with conventional hydrocarbon fuels, and its high acidity (the total acid number is in the range ~100 – 200, whereas a TAN lower than 2 is required for most transport vessels).

Reference: Resende (2016).

4. False. According to D'Jesús *et al.* (2006), potassium improved the yield of supercritical-water treatment of corn starch – increasing potassium concentration from 0 to 500 ppm led to an increase in gasification yield from 0.82 to 0.92 – but had no influence on the processing of clover grass and corn silage, possibly because these products already have substantial amounts of K in their natural composition.

Reference: D'Jesús *et al.* (2006).

5. False. Waheed and Williams (2013) actually reported that the highest hydrogen yield of 25.4 mmol g⁻¹ of biomass was obtained from the pyrolysis/reforming of rice husk, not sugar cane bagasse, using 10 wt% Ni-dolomite. The highest hydrogen concentration in the gas mixture was 59.14 vol%.

Reference: Waheed and Williams (2013).

6. False. Okolie *et al.* (2019) note that although the use of nickel in SCWG could possibly lead to high total gas yields and improved carbon gasification efficiency, the H₂ production is diminished due to consumption in secondary hydrogenation reactions. Another issue with nickel catalysts in SCWG is the unavoidable problem of sintering and catalyst deactivation by tar-forming products.

References: Cao *et al.* (2020); Okolie *et al.* (2019).

7. True. Indeed, Ozbas *et al.* (2019) noted that the R² values for hydrogen prediction in the four regression techniques were all greater than 0.90. The best performance came from linear regression, for which a R² of 0.999 was reported.

Reference: Ozbas *et al.* (2019).

8. True. This statement refers to the classification proposed by Milne *et al.* (1998), who classified tars depending on reaction regimes as 'primary products,'

which are characterized by cellulose-derived, hemicellulose-derived and lignin-derived products; 'secondary products,' which are characterized by phenolics and olefins; 'alkyl tertiary products,' which are mainly methyl derivatives of aromatic compounds; and 'condensed tertiary products,' which are polycyclic aromatic hydrocarbons without substituent groups. In general, tertiary tars and primary tars do not coexist, because tertiary tars only appear after primary tars are completely converted into secondary tars.

Reference: Milne et al. (1998).

9. False. While it is true that formation of tar is a major hurdle for the practical implementation of biomass gasification, the meta-analysis conducted by Safarian *et al.* (2019) noted that less than 12% of all model-driven studies included any tar modelling whatsoever. What's more, the few studies that accounted for tar formation incorporated it as a single, or very few, representative compound(s), which is a gross oversimplification since tar consists of a complex mixture that varies greatly depending on the process' operating conditions, feed, and gasifier type.

Reference: Safarian et al. (2019).

10. True. Pinto *et al.* (2015) reported that dolomite was the material that showed the highest catalytic activity, as the lowest tar formation and the highest H₂ gas yield were observed in the presence of this catalyst.

Reference: Pinto et al. (2015).

11. False. Plasmas can be divided into thermal and non-thermal/non-equilibrium, depending on temperature, energy level, and electronic density. For thermal plasma, the gases can reach a temperature of well over 1700°C, and all energetic and neutral species are in equilibrium. These exceedingly high temperatures make it hard to combine thermal plasmas with heterogeneous catalysts, hence most tentative HCPS formulations have resorted to non-thermal plasmas.

Reference: Liu et al. (2019).

12. True. In contrast to hydrochar, torrefied biomass is generally not as suitable for pelletization, typically requiring an additional binder to produce acceptable pellets. Formation of robust pellets to facilitate handling, storage, and transport of compressed char is critical to solid biofuel applications.

References: Hoekman et al. (2013); Reza et al. (2012).

13. False. In actuality, Li *et al.* (2013) reported that the presence of packaging materials in the fuel had a significant influence on the energy content of the recovered solids. As the proportion of packaging materials increased, the energy content of recovered solids decreased because of the low energetic retention associated with the packaging materials. Still, it is worth noting that most of the fuel combinations tested by Li's group, including those that included a substantial proportion of packaging materials, were associated with a net positive energy balance.

Reference: Li et al. (2013).

14. True. Indeed, Hoekman *et al.* (2013) reported increases in energy density with increasing temperature. Energy densification, they noted, increased with process temperature due to preferential loss of oxygen. All raw biomass feedstocks had O/C ratios in the range of 0.61 – 0.74. As process temperature increased, these ratios decreased and converged to a value of approximately 0.2 at HTC temperatures of $\geq 275^{\circ}\text{C}$.

Reference: Hoekman et al. (2013).

15. False. Although Reza *et al.* (2014) were not able to perform a thorough analysis of water production because of an incomplete analysis of volatiles in their experimental setup, some observations could be made. A net consumption of water was observed at 200°C, indicating that hydrolysis is more prominent than dehydration at low temperature. As temperature was increased from 230 to 260°C, a net *increase* of water was verified, possibly due to dehydration or retro-aldol condensation of cellulose.

Reference: Reza et al. (2014).

16. False. In actuality, fungal pretreatment is sluggish, as a long operational time may be required to achieve even an average lignin removal and cellulose saccharification. Concerns have been raised about increased costs and contamination due to the very long pretreatment times associated with this process.

Reference: Wan and Li (2012).

17. False. As noted in a review by Loow *et al.* (2016), the most common dilute mineral acid used in DAH is sulfuric acid, H₂SO₄. Nitric acid (HNO₃), hydrochloric acid (HCl), phosphoric acid (H₃PO₄), and some organic acids have also been investigated.

Reference: Loow *et al.* (2016).

18. True. According to Ma *et al.* (2010), the reducing sugar yield from enzymatic hydrolysis of co-treated sample was 1.13 to 2.11 times greater than that of acid-treated sample at the same conditions. Likewise, the ethanol yield from combined pretreatment increased 1.34-fold relatively to that obtained from acid pretreatment alone.

Reference: Ma *et al.* (2010).

19. True. As reviewed by Loow *et al.* (2016), ammonia-based processes such as AFEX and ammonia recycling percolation (ARP) have relatively high sugar yields – although products usually occur in oligomeric form – and low inhibitor production for downstream processes. Since the amount of inhibitors generated is low, the biomass washing step after pretreatment can be avoided.

Reference: Loow *et al.* (2016).

20. False. While treatment with diethyl-, triethyl-, and diisopropylammonium ILS indeed resulted in high saccharification yields, it was triethylammonium hydrogen sulfate that led to the highest glucose yield, achieving a 75% efficacy compared to a [C₂C₁im][OAc]:[H₂O] mixture. Diethylammonium hydrogen sulfate came second, yielding 67% of the saccharification output of a [C₂C₁im][OAc]:[H₂O] mixture.

Reference: George *et al.* (2015).

21. False. Much to the contrary, García-Cubero *et al.* (2009) reported that in the trial where sodium hydroxide was added, cellulose degradation increased by up to 40% for rye straw and 50% for wheat straw. They noted that authors before them had reported that under basic conditions hydroxide ions catalyze the decomposition of ozone to yield highly reactive and non-selective hydroxyl radicals, causing delignification to decrease and degradation of cellulose and hemicellulose to increase.

Reference: García-Cubero *et al.* (2009).

22. False. Teghammar *et al.* (2012) actually reported that nearly 98% of NMMO could be recovered after application in all three feedstocks, which suggests that this approach is more economical than previously thought. The fact that low temperatures (~130°C) were needed for the NMMO pretreatment adds to the feasibility of this technique as an accessible means to boost biofuel production.

Reference: Teghammar *et al.* (2012).

23. True. Part of the statement is taken verbatim from section 6 of Tchapda and Pisupati (2014). Of course, the gross calorific value and other thermochemical variables of a complex entity such as a coal-biomass blend are not dependent solely on composition. Cold gas efficiency and the gross calorific value are also augmented by temperature, increasing up to an optimum temperature above which they begin to decrease.

Reference: Tchapda and Pisupati (2014).

24. True. In the index framework proposed by Oladejo *et al.* (2017), a synergy factor $SF > 1.15$ is associated with a synergistic fuel blend; in turn, $0.8 \leq SF \leq 1.15$ is associated with additive behavior; finally, a value of $SF \leq 0.8$ suggests deteriorated combustion performance after blending. The most significant synergistic effect reported by Oladejo's group occurred for a mixture of 70 wt% Yunnan coal + 30 wt% oat straw, for which $SF = 1.50$.

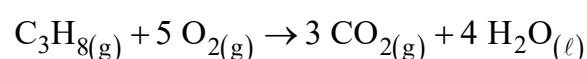
Reference: Oladejo *et al.* (2017).

25. True. According to Arán *et al.* (2016), the copper retention capacity increased with the pH of the medium for both rice husk and chicken manure biochars. Arán's group noted that this effect of pH on the adsorption of metals on BC has been reported by other authors and appears to be linked to the effect observed for other carbon-rich materials, such as activated carbon and humic substances.

Reference: Arán *et al.* (2016).

■ Problem 4

The chemical equation that describes the combustion of propane is



Accordingly, the enthalpy of reaction for the process above is

$$\Delta H_R = 3\Delta H_f^\circ[\text{CO}_2] + 4\Delta H_f^\circ[\text{H}_2\text{O}] - \Delta H_f^\circ[\text{C}_3\text{H}_8] - 4\Delta H_f^\circ[\text{O}_2]$$

$$\therefore \Delta H_R = 3 \times (-393.5) + 4 \times (-285.8) - 104.7 - 4 \times 0 = -2430 \text{ kJ mol}^{-1}$$

$$\therefore \Delta H_R = -2430 \times 10^3 \text{ kJ kmol}^{-1}$$

Since the molar mass of propane is 44 kg kmol^{-1} , the lower heating value is found as

$$LHV = \frac{2430 \times 10^3}{44} = \boxed{55,230 \text{ kJ/kg}}$$

When 4 moles of water vapor in the products condense to water, the enthalpy of reaction becomes

$$\Delta H_R^* = -2430 \times 10^3 - 4 \times 44,000 = -2606 \times 10^3 \text{ kJ kmol}^{-1}$$

and the higher heating value is found as

$$HHV = \frac{2606 \times 10^3}{44} = \boxed{59,230 \text{ kJ/kg}}$$

◆ The correct answer is **C**.

■ Problem 5

We first compute the Spalding transfer number:

$$B_q = \frac{c_p(T_\infty - T_s)}{h_{fg}} = \frac{2240 \times (500 - 400)}{300,000} = 0.747$$

It is usual to take a weighted thermal conductivity

$$k = 0.4k_F(\bar{T}) + 0.6k_\infty(\bar{T})$$

where k_F is the thermal conductivity of fuel, k_∞ is the thermal conductivity of the quiescent medium, and \bar{T} is an average temperature given by

$$\bar{T} = \frac{T_{\text{boil}} + T_\infty}{2} = \frac{400 + 500}{2} = 450 \text{ K}$$

so that

$$k = 0.4 \times 0.033 + 0.6 \times 0.04 = 0.0372 \text{ W/m} \cdot \text{K}$$

Then, we determine the evaporation constant K :

$$K = \frac{8k}{\rho_l c_p} \ln(1 + B_q) = \frac{8 \times 0.0372}{703 \times 2510} \times \ln(1 + 0.747) = 9.41 \times 10^{-8} \text{ m}^2/\text{s}$$

The droplet lifetime follows as

$$t_d = \frac{D_0^2}{K} = \frac{(850 \times 10^{-6})^2}{9.41 \times 10^{-8}} = \boxed{7.68 \text{ sec}}$$

The droplet will be fully vaporized within less than 7.7 seconds.

◆ The correct answer is **B**.

■ Problem 6

The total energy required in the ethanol production plant is

$$E_{\text{plant}} = 1.2 + 9.2 + 4.5 + 0.4 = 15.3 \text{ GJ}$$

The corn feedstock required to produce 1000 liters of ethanol is $2.4 \times 1000 = 2400 \text{ kg}$. The required farm area follows as

$$A_{\text{corn}} = \frac{2400}{9280} = 0.259 \text{ ha}$$

The energy required to cultivate this area of corn is determined as

$$E_{\text{corn}} = (4.6 + 5.9 + 8.2 + 4.0) \times 0.259 = 5.88 \text{ GJ}$$

The total energy input is then

$$E_{\text{input}} = E_{\text{plant}} + E_{\text{corn}} = 15.3 + 5.88 = 21.2 \text{ GJ}$$

The total energy available in 1000 liters of ethanol is

$$E_{\text{available}} = 22 \times 1000 = 22,000 \text{ MJ} = 22 \text{ GJ}$$

Finally, the net energy balance ratio is

$$NEB = \frac{E_{\text{available}}}{E_{\text{input}}} = \frac{22}{21.2} = \boxed{1.038}$$

That is, in the case at hand the available energy afforded by the corn ethanol is about 3.8% greater than the energy input required to produce it.

◆ The correct answer is **A**.

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