A review of biomass gasification modelling

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Abstract

Currently around 10% of all energy generated worldwide comes from biomass. Most of this 10% is biofuel energy from the fermentation of corn and sugarcane. Fermentation of corn competes with the global food supply, and fermentation of sugarcane drives deforestation. Therefore, the renewable and sustainable growth of these two bio-based energy sources may not be desirable even if it is economically feasible. Biomass gasification by contrast is significantly more flexible in terms of the bio-feedstock or waste that can be processed to either produce biofuels or to co-generate electricity and heat on demand. This superior flexibility of gasification both in terms of the feedstock type and also the energy generation or fuel production options, is what drives expanding research and implementation opportunities for biomass gasification. Research progress is accelerated by modelling work. This review is the first review in the biomass gasification modelling field to collect and analyze statistics on the growing number of gasification modelling studies and approaches used. The frequency of the various modelling choices made, and the trends this data reveals, is reported. For new researchers this review provides a succinct guide to the modelling choices that needs to made early on in a modelling study or project. A detailed methodology characterization is introduced that includes consequential modelling choices not explicitly addressed by prior reviews. To seasoned researchers this study provides the first statistical (as opposed to ad hoc or anecdotal) picture of what their fellow researchers are doing. The data to be presented reveals that even though the availability of kinetic data increased over the last two decades, the fraction of simulations that utilize kinetic modelling (as opposed to pure equilibrium calculations) decreased from roughly 50% to around 25% over the last decade.

Keywords: Biomass; Gasification; Equilibrium model; Stoichiometric model; Kinetic model; Tar

1. Introduction and objectives

Currently, about 81.4% of the world's primary energy requirements are supplied by the big three fossil fuels (oil, coal and natural gas). The next biggest contribution, approximately 9.7%, is derived from biomass (primarily ethanol and biodiesel) and waste. The remainder of the world's energy needs is supplied by nuclear (~ 4.9%), hydroelectric (~ 2.5%) and the trio of rapidly growing renewables geothermal, solar and wind that currently account for ~ 1.5% [1-3].

Using fossil fuels to produce energy has negative social, political, and environmental impacts, and the burning of fossil fuels has increased global CO_2 concentrations and further intensified climate change [4-7]. These consequences are strong motivators for the development of renewable and domestically available energy sources [8]. Among the various renewable energies, biofuels from biomass have seen large-scale implementation (especially sugarcane ethanol in Brazil and corn ethanol in the US) as transportation fuels, allowing for more fuel security and the creation of new job opportunities. As can be seen from the world energy statistics in the opening paragraph biofuel and waste already are surprisingly large source of the world energy supply with the waste-to-energy sector growing and developing rapidly [7, 9].

Extracting energy from biomass or organic solid waste requires biochemical and/or thermochemical processes [10]. During biochemical processes like fermentation, biomass is converted to biofuels through the digestive action of living organisms. However, in thermochemical processes, biomass is converted to biofuels, gases, and chemicals by applying heat and/or pressure. Gasification, also widely used to gasify coal and natural gas, is the most prominent thermochemical biomass-to-energy and waste-to-energy conversion processes gaining ever more research and commercial interest [9]. In addition to producing syngas from biomass for subsequent biofuel synthesis, gasification typically achieves superior efficiency for electricity generation compared to more conventional alternatives such as incineration (to generate steam for turbines). Electricity production utilizing gasification extracts more electricity per kilogram of biomass [11] or per kilogram of municipal waste [12-14] compared with alternatives such as incineration or biogas from digesters. Using gas engines, gas turbines or fuel cells, electricity can easily be generated from syngas with existing or marginally modified infrastructure. In certain situations, the superior energy extraction efficiency of gasification does result in the lowest cost (compared with conventional technologies) in per unit of energy produced from biomass [11, 15]. Hence, the thermochemical or gasification route between raw biomass and energy is significantly more flexible than the currently dominant biochemical route – predominantly the fermentation of corn or sugar cane to ethanol. Gasification can economically transform many more types of biomass compared to fermentation. Demonstrated feedstock include most types of organic waste, sea-weed and forestry waste. The syngas produced from any of these sources is readily processable into liquid fuels or can fire the efficient co-generation of heat and electricity. It is on account of this superior flexibility of gasification, both on the feedstock end and energy generation end, that gasification will likely play an ever increasing role in our future energy mix.

The performance of the process can be influenced by many factors, including feedstock, process design, and the operating parameters [16]. As a result, gasifier reactors need to be designed either by experimental data and/or by using mathematical or simulation based modelling of the gasification process. The experimental option, though the most reliable, is best utilized in combination with modelling [17]. In practice modelling always play a key role both in applied gasification R&D work or in more fundamental research studies. When it

comes to the applied work models that are validated through experiments do reliably predict gasifier performance as a function of feedstock and give qualitative and quantitative information for prospective practical operations. Modelling is very effective in optimizing the operation of an existing gasifier, as well as in exploring operational limits and gaining insight into the relationship between operational parameters and in explaining trends in the data. [18]. Simulations also serve as a low-cost method for exploring the potential benefits, costs, and risks associated with the implementation of gasification given the fact that time and budgets for experimentation and pilot data collection are always finite [17].

When it comes to more fundamental research aimed at understanding mathematical models and simulations have been used extensively as well by researchers and equipment manufacturers. Moreover, only the combination of experiments and process modelling can provide an understanding of the physical and chemical phenomena within the gasifier.

However, the range of complexity and detail that can be included, or omitted, in any gasifier model is large. A detailed fine-grained simulation of the gasification process involves the modelling of heat and mass transfer, multiphase fluid dynamics, chemical transport and multiple heterogeneous and homogenous chemical reactions. Both applied and scientific modelers need to make a large number of choices regarding modelling type and what to include and what to omit or approximate.

By now, there is a substantial body of literature utilizing models of various types of gasifiers that have different degrees of complexity. However, reviews of these modelling and simulation studies are somewhat limited [17]. Our review found seven other reviews, which may sound sufficient if not for the fact that there is a significant amount of repetition among several of them [17, 19-24]. There is a particular need for reviews that are not just a catalogue of types of models and prior studies but that instead systematically compare modelling approaches and answer important questions about what is known about the relative merits of these modelling approaches. For example, the current review is the first to address whether or not stoichiometric and nonstoichiometric models lead to identical predictions or not. The present review is also the first to consider the more consequential choices that a modeler has to make, namely whether to use a total equilibrium or semi-equilibrium approach (see section 4). Another feature of the current study that differs from prior reviews is the inclusion of representative statistics indicating the frequency of the use of the various competing modelling choices in the literature to date.

Finally, the existing review articles do not address the recent progress made in the area of tar modelling. The results of the current review confirm that the vast majority of gasification models and simulations treat tar in gasification in one of three ways, namely as either not present in the gas phase (i.e. absent or negligible), present but inert, or where all tar species are modeled by a single (or a couple of) representative model compound(s) (with aromatics such as benzene or naphthalene, the most typical choices) [25]. Of course, all three options are a vast oversimplification, but in all three cases, the vital question to the researcher or

engineer is how large the error incurred is with a given simplification in a given application. In the past, it is likely that these simplifications were primarily motivated not by the certain knowledge that the error incurred was acceptably small, but rather by the fact that tar is complex, and its composition and reactivity varies according to the process operating conditions [26]. Furthermore, the experimental characterization of the tar species present within and during gasification is very limited, which is in part because of the difficulty of sample extraction and analysis [20]. A review that includes a survey of what is known about the answer to these questions in various scenarios should be practically useful. In addition, for those scenarios where a more sophisticated tar treatment would make a worthwhile or critical difference, new tar models and treatment approaches have been developed in recent years [20, 25, 27] These tar models are included in the current review. In the present work, a comprehensive study of the developed models and a new classification of the most important gasification modelling approaches is introduced. Frequency of use statistics is presented. Finally, tar modelling and its approximation methods are surveyed.
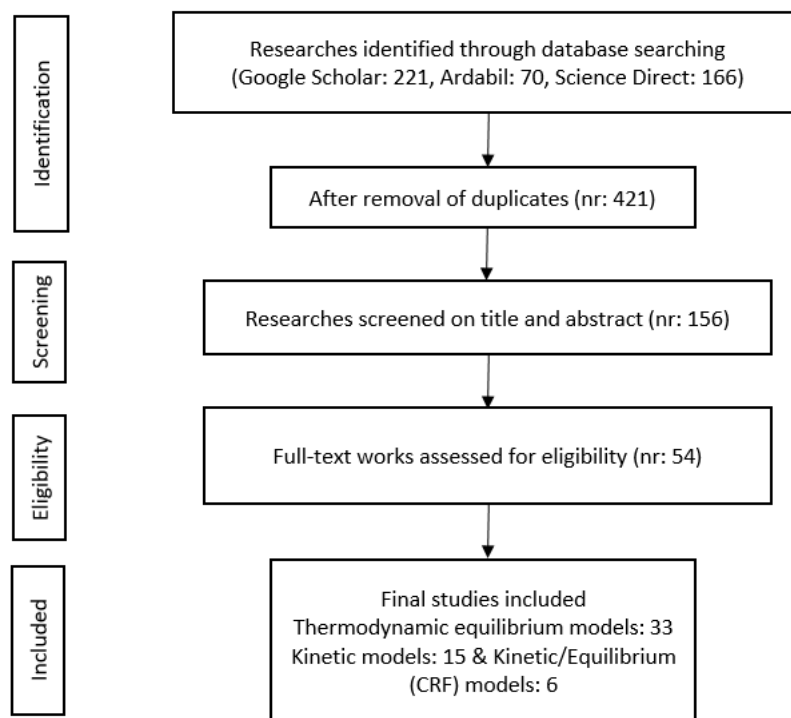
2. Methodology of article selection

Fig. 1. Flow diagram depicting the details of the literature search

This section describes the systematic search strategy (outlined in Fig. 1) followed to select articles for inclusion in the statistics and discussion in this review. As a starting point three databases, namely Google Scholar, Ardabil Science and Science Direct were searched for keywords gasification and modelling or modeling. This search strategy yielded 457 results.

After removing duplicates and any review articles, the total dropped to 421 works. The next step is to identify and filter out and retain just articles with focus on, overlap with, or relevance to biomass gasification. Screening the articles with these criteria revealed 156 publications that met the criteria based on their titles and abstracts and another four articles were provisionally included after screening the references of the relevant articles by hand. Further assessment of eligibility based on full-text works led to 54 studies being selected, with 33 studies on thermodynamic equilibrium models, 15 works on kinetic modelling, and 6 studies on kinetic/equilibrium (CRF) modelling. One aim of the current review was to provide a better understanding of the prevalence of these approaches. The relative prevalence of these main modelling approaches over time is shown in Fig. 2 [10, 16, 25, 28-93]; in Fig. 2, it can be seen that thermodynamic equilibrium modelling has been favored to date and is currently the chosen approach in roughly 60% of models and simulations published to date. What our survey suggests, perhaps for the first time, that equilibrium models are perhaps not just chosen because of a lack of kinetic data, as is sometimes assumed. This conclusion is suggested by the fact that our statistics show that although the amount of mechanistic and kinetic data has grown steadily since 2006, the fraction of simulation and modelling studies that chose kinetic over equilibrium models has not grown together with the availability of kinetic data. In fact, the fraction of modelling studies that use equilibrium only approaches have actually increased from a low in the period 2006-2009 (around 50% of models) to being the chosen modelling approach in about 75% of biomass modelling articles from 2014 to 2017.
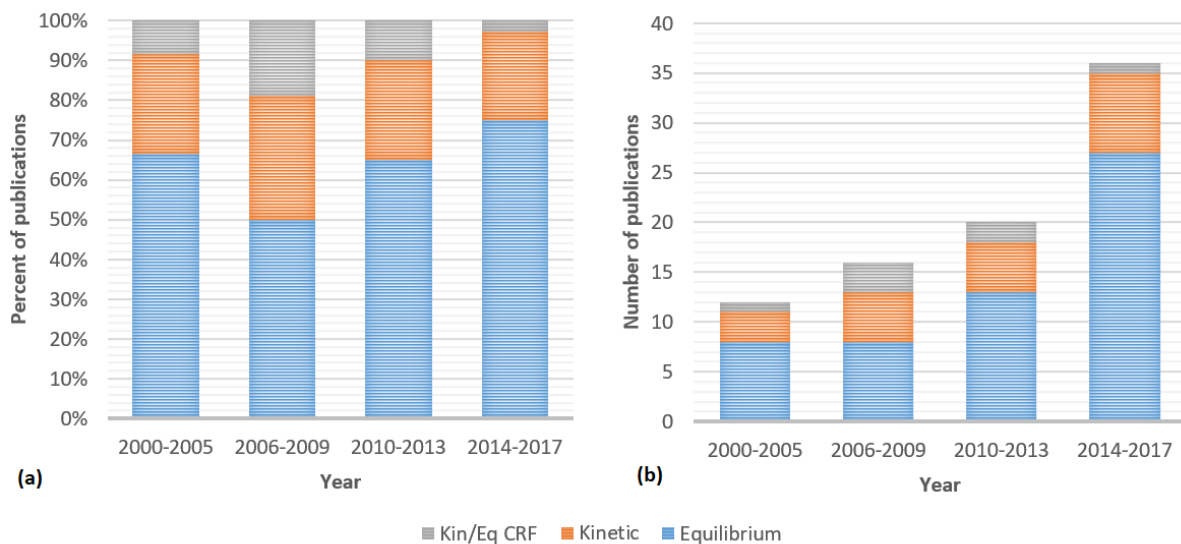

Fig. 2. Overview of gasification models since 2000, (a) as percent, (b) absolute number of studies

3. Gasification process and technologies

3.1. Gasification process overview

Gasification is the conversion of solid or liquid feedstock into syngas. The syngas is used as a chemical feedstock or is utilized directly as a fuel to generate heat, electricity, or both. The gasification process consists of the following stages: drying, pyrolysis, oxidation (combustion), reduction (char gasification), and cracking (Fig. 3) [94].
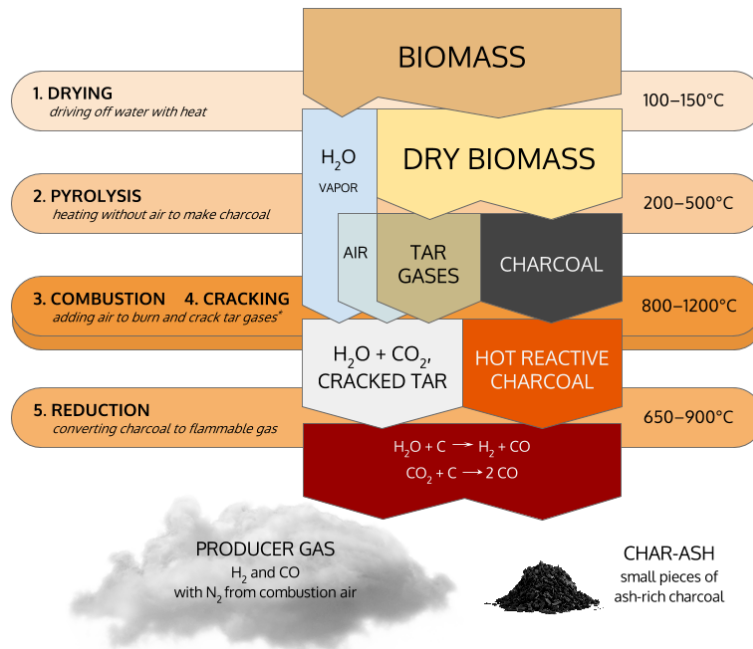

Fig. 3. Gasification process steps (Reprinted from www.allpowerlabs.com, Copyright 2018 All Power Labs, with permission from All Power Labs)
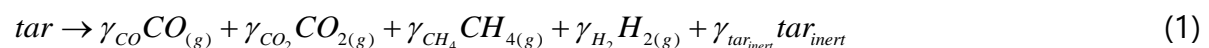
Typically, the moisture in the biomass feed ranges from 5–35% that during drying step, it is reduced to below 5%. In the pyrolysis step, the biomass is heated from 200 up to 700 °C with limited oxygen or air. Under these conditions the volatile components in the biomass are vaporized. The volatile vapor is a mixture of hydrogen, carbon monoxide, carbon dioxide, methane, tar (heavier hydrocarbon) gases, and water vapor [95]. Tar (a black, viscous, and potentially corrosive liquid at standard temperature and pressure that is predominantly composed of heavy organic and inorganic molecules) and char (a solid residue mainly containing carbon) are also produced during pyrolysis [96]. The oxygen supplied to the gasifier reacts with the combustible substances, producing CO_2 and H_2O. Some of this CO_2 and H_2O subsequently are reduced to CO and H_2 upon contact with the char produced from pyrolysis [18]. Moreover, the hydrogen in the biomass can be oxidized, generating water. The reduction reactions occurring inside the gasifier are endothermic, and the energy required for these reactions is provided by the combustion of char and volatiles. Reduction of the biomass yields combustible gases such as hydrogen, carbon monoxide, and methane through a series of reactions; the main reactions in this category are as follows [19, 96]:
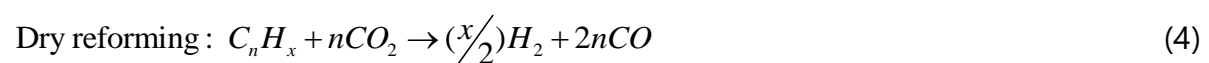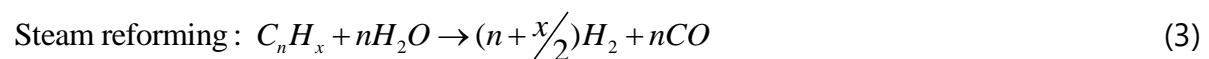
Table 1

Main gasification reactions [19, 96]

Heterogeneous reactions		
$C + O_2 \rightarrow CO_2 + 394$ kJ/mol	Complete combustion	R1
$C + 0.5O_2 \rightarrow CO + 111$ kJ/mol	Partial combustion	R2
$C + CO_2 \rightarrow 2CO$ -172 kJ/mol	Boudouard	R3
$C + H_2O \rightarrow CO + H_2$ -131 kJ/mol	Water-gas	R4
$C + 2H_2 \rightarrow CH_4 + 75$ kJ/mol	Methanation	R5
Homogeneous reactions		
$CO + 0.5O_2 \rightarrow CO_2 + 283$ kJ/mol	CO partial combustion	R6
$H_2 + 0.5O_2 \rightarrow H_2O + 242$ kJ/mol	H₂ combustion	R7
$CO + H_2O \rightarrow CO_2 + H_2 + 41$ kJ/mol	Water-gas shift (WGS)	R8
$CH_4 + H_2O \rightarrow CO + 3H_2$ -206 kJ/mol	Reforming	R9
H₂S and NH₃ formation reactions		
$H_2 + S \rightarrow H_2S$	H₂S formation	R10
$3H_2 + N_2 \rightarrow 2NH_3$	NH₃ formation	R11

Moreover, the tar gases produced during the pyrolysis step undergo cracking in the gasification step, which produces a mixture of non-condensable gasses, light hydrocarbons, and unconverted tar. This process is represented by equation 1, with γ showing the yield coefficients of the product gasses and unconverted tar. The values of the γ coefficients depend strongly on gasifier operating parameters and feedstock type. However, it is treated as a constant in some works [25]. The most important parameters determining the γ coefficients are temperature, pressure, gasifying medium, catalyst and additives, equivalence ratio (ER), and residence time.

$$tar \rightarrow \gamma_{CO}CO_{(g)} + \gamma_{CO_2}CO_{2(g)} + \gamma_{CH_4}CH_{4(g)} + \gamma_{H_2}H_{2(g)} + \gamma_{tar_{inert}}tar_{inert} \tag{1}$$

An example of a relatively more detailed account of tar cracking, steam and dry reforming, and carbon formation was developed by Devi et al. [26]. Their model utilizes the following reactions:

$$\text{Cracking}: pC_nH_x \rightarrow qC_mH_y + rH_2 \tag{2}$$

$$\text{Steam reforming}: C_nH_x + nH_2O \rightarrow (n + x/2)H_2 + nCO \tag{3}$$

$$\text{Dry reforming}: C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO \tag{4}$$

$$\text{Carbon formation}: C_nH_x \rightarrow nC + (x/2)H_2 \tag{5}$$

Where C_nH_x represents tar and C_mH_y represents dehydrogenated hydrocarbons.

Endothermic reactions decrease the temperature in the reduction zone and the temperature further falls downstream from the gasifier. As a result, most of the tar condenses out in these segments. The resulting tar deposits block and foul engines and turbines, downstream reactors, the syngas conditioning and filtration system. Several efficient methods have been employed to achieve tar removal from the outlet gas. Tar removal technologies can be divided into two approaches: hot gas cleaning after the gasifier (secondary methods) and treatments inside the gasifier (primary methods). Secondary techniques are conventionally used for the treatment of the hot product gas from the gasifier. Tar reduction can be achieved either chemically by using a catalyst or physically by using a cyclone, baffle filter, ceramic filter, fabric filter, rotating particle separator, electrostatic filter, or scrubber. In the primary treatment, the gasifier is optimized to produce a product gas with minimum tar concentration. The different primary treatment approaches are (a) the appropriate selection of operating parameters, (b) use of a bed additive or catalysts, and (c) gasifier modifications. The operating parameters such as temperature, gasifying agent (e.g., air, pure steam, or steam$-O_2$ mixtures), ER, and residence time play an important role in tar formation and decomposition. By using some active bed additives such as dolomite, olivine, or char inside the gasifier, it is possible to improve the gasifier's performance.

As mentioned, in the pyrolysis step, heat provided by combustion heats the dry biomass to the point that it decomposes into solid char and volatiles (tar and gases). The sum of the tar and gases are equal to the volatile matter (VM), the amount of which is typically quantified using a proximate analysis [25]. The VM percent for different kinds of woody biomasses is high relative to coal, with biomass VM typically in the range of 70–90% by mass. Moreover, char is often modeled as consisting of carbon only, and its amount would be equal to the fixed carbon extracted from the proximate analysis [55]. The typical mass fraction division of the streams within the pyrolysis and gasification steps is depicted in Fig. 4. The mass flow distribution in this illustrative example are based on the gasification of Olive Wood in a fixed bed downdraft gasifier with air as agent, as reported by [30]. It can be seen that in this particular case, well more than 90% of a downdraft gasification input mass end up in the syngas product stream, while the final tar content in our example is about 0.1% (in general it ranges from 0 to 5%) of the inserted wood material. Hence, the tar amount can be almost negligible in many applications especially if pyrolysis tar is combusted, cracked and reduced.

Pyrolysis of biomass and wood gasification produce about 10 to 30 wt% char and tar in (e.g. [97]). The 10 wt% char and 5 wt% tar produced from olive wood pyrolysis reported by [30], which is shown in Fig. 4, may be on the low end. The amount of tar that exits either with the product gas, or condenses out on downstream components, depends significantly on the gasifier type and operating conditions and even factors such as the amount of char present in the reduction zone (which can be catalytic for tar cracking and reduction [97-99]). For example, Baker et al. conducted an early survey that found tar yield up to 12 wt% for some

updraft gasifiers and in the range of 4–15 wt% for fluidized bed gasifiers, with the higher end observed at lower temperatures (600 °C) [99]. Downdraft gasifiers operating at a relatively higher temperature of 900 °C tend to perform well in terms of final tar yield, with a final tar yield less than 1 wt% common [30, 99].
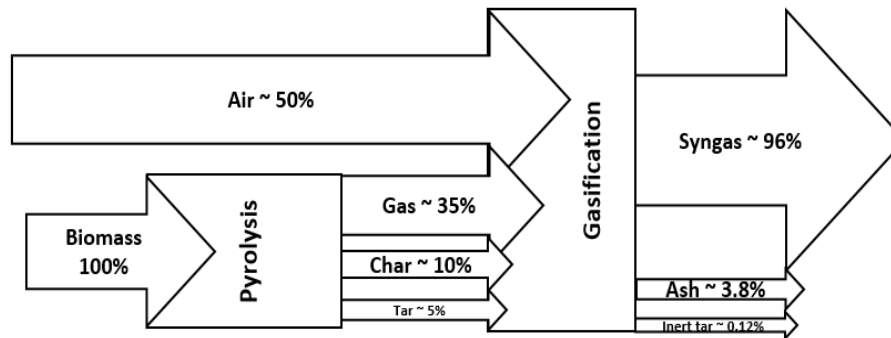

Fig. 4. A Sankey chart of mass flow distribution throughput biomass gasification

3.2. Gasification technologies for biomasses

Gasifiers can be divided into two principal types of fixed beds and fluidized beds.

- Fixed-bed (updraft, downdraft, cross-draft): The fixed-bed gasifier category includes gasifiers with a bed filled by solid fuel particles where the gasifying media and gas either are rising (updraft), descending (downdraft), or flowing horizontally through the reactor (cross-draft) [19]. The gasifying media may be air, steam, oxygen, or a mixture of them. The two main practical advantages of fixed-bed gasifiers are that they are relatively more cost-effective for small-scale applications and tend to produce a clean product gas with low dust and low tar content when compared with fluidized bed alternatives [100]. The main disadvantage is that they can have poorer heat transfer and temperature inhomogeneity, and they do not scale up as well as fluidized bed gasifiers. Secondly, fixed-bed gasifiers typically require tighter feed specifications – for example a moisture level below 20% and a fairly uniform particle size distribution with few fines for the biomass (to prevent clogging and channeling).
- The fluidized bed (bubbling, circulating): A typical fluidized bed is a cylindrical column that contains particles and through which fluid—either gaseous or liquid—flows. The velocity of the fluid is sufficiently high enough to suspend the particles within the column, providing a large surface area for the fluid to make contact with, which is the chief advantage of fluidized beds. The main potential advantages of fluidized beds are their superior heat and material transfer between the gas and solid phases. Thus, a fluidized bed maintains a homogeneous temperature field and is more flexible in the sense of wide variations in fuel quality. The main downside of fluidized bed gasifiers is

that they tend to produce more dust and particulates in the product gas, which can present a significant problem for downstream equipment [101].

4. Biomass gasification models

The main two categories of gasification models are equilibrium and kinetic models. This survey of gasification modelling choices found that roughly 66% biomass gasification simulations utilize some type of equilibrium model, and the remaining 34% utilize some type of kinetic model (see Fig. 5). This section will discuss the main variations of both these approaches, but first a brief review of reasons for modelling and simulating biomass gasification are studied. Moreover, features and weakness of these methods are gathered in Table 2 [17, 19, 23].

A gasification plant operator needs to optimize the feedstock flow rate, agent flow rate, equivalence ratio, reactor pressure, and temperature to achieve a desirable syngas composition and yield. Changes in any of these parameters can have a substantial impact on the product compositions and the gasifier performance [23]. Moreover, the admissible range for feedstock properties is rather narrow because the chemistry and fluid dynamics of gasification are very sensitive to variations in feedstock composition, moisture, ash content, particle size, and density [23]. In practice, laboratory experiments, pilot facilities, and field experience can and do provide information regarding the optimum conditions and appropriate feedstock for a reactor, but these lessons can be more time-consuming and expensive compared with modelling.
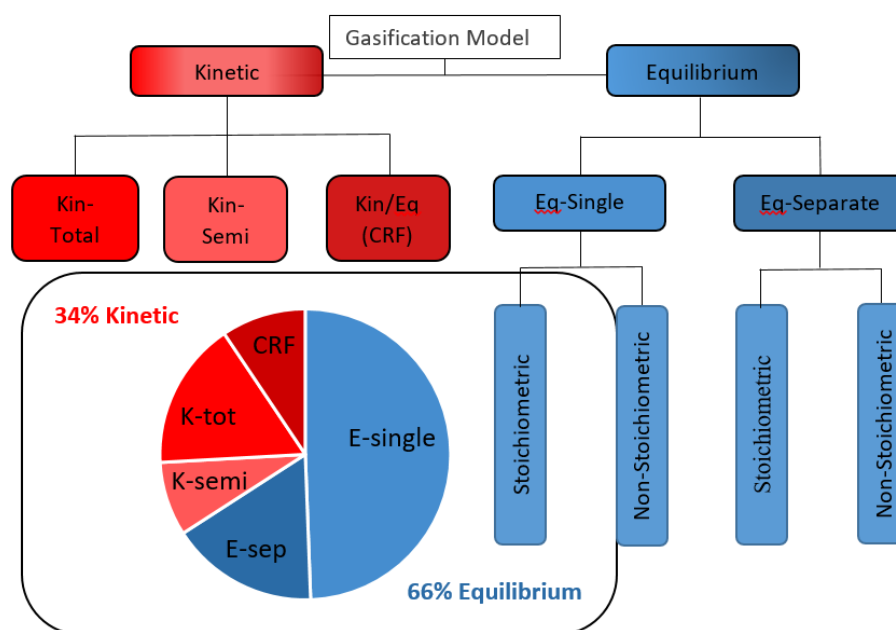

Fig. 5. A categorization of gasification model types

A higher degree of insight and economic efficiency can be obtained by combining mathematical modelling and process simulation with physical experimentation. A good model

should give a reasonably accurate representation of the chemical and physical phenomena occurring inside the gasifier reactor. One approach to ensure the predictive ability of a model is to strive to include all reactions and transport phenomena as realistically as possible. However, in practice, modelers invariably must ignore some of the details and make simplifying assumptions that decrease the complexity of the model. Thus, practically all models inevitably will be approximations, and the question is just how good of an approximation a given model is. A good example of the unavoidable need for simplification is tar formation and cracking. The number of detectable hydrocarbon species within a tar sample, and the number of relevant formation, conversion reactions can be in the hundreds [20]. As a result of this complexity, many models ignore tar modelling altogether. In our survey just under 12% of all published biomass gasification simulations included any tar modelling. Notwithstanding the fact that minimizing tar is a practically and operationally important objective—tar either condenses out in the downstream equipment and reducing its performance, or pollutes the product syngas. Whenever tar is included, it is always in a simplified form compared to reality.

Table 2
Features and weakness of gasification modelling approaches

	Features	Weakness
Equilibrium modelling	- Simple method - Not required to consider chemical reactions - Useful tool to evaluate a complex reacting system that is difficult or unsafe to produce experimentally or in commercial operation - Predicts the maximum achievable yield of the products - Very useful in the predicting of downdraft gasifiers - Useful tool for a preliminary comparison of fuels and process parameters - Independent of gasifier design - Flexible for various feedstocks and process parameters - Good representation for high temperatures (750–1000 °C) - Can be improved by using the coefficients for equilibrium constants or yields distribution	- Tars are not considered - Heat loss is neglected - Not fully attained for low operation temperatures - Limitation is for fluidized bed gasifiers - Cannot give highly accurate results for all cases

| Kinetics modelling | • Consideration of finite time or finite volume
• Accurate and detailed results
• Good approximation at low temperatures
• Includes both reactions kinetics and hydrodynamics inside the gasifier
• Very useful tool for the evaluation of particle size impact
• Proper for fluidized bed gasifiers
• Able to predict the product composition at different positions along a reactor | • Sensitive to the gas–solid contacting process
• Computationally intensive
• Limits their applicability to different plants |

4.1. Thermodynamic equilibrium models

The thermodynamic equilibrium approach predicts the composition of the outlet gases based on the assumption that the components react in a fully mixed condition for an infinite period of time [23, 24]. A less strict—and more practical—definition of the set of assumptions that would justify the use of an equilibrium modelling approach in a real gasifier is when the following conditions are met:

1) Reactant residence time (τ_{res}) in the reduction zone is long compared to the half-life ($\tau_{1/2}$) of all reactants. In essence $\tau_{res} \gg \tau_{1/2}$, with $\tau_{1/2}$ a time scale determined by the reaction rates of the rate limiting reaction (s),
2) the temperature in the reduction zone can be assumed as constant, and
3) chemical mixing is close to perfect.

Thermodynamic equilibrium calculations are simple compared with kinetic models and independent of the gasifier design, and in the simplest, most ideal case, general thermodynamic properties can be used for equilibrium modelling, while a larger set of hard-to-come-by and accurate kinetic parameters is needed for kinetic modelling. These considerations render equilibrium modelling the more convenient method with which to study the general relations between fuel and process parameters and limiting syngas composition and yield. However, thermodynamic equilibrium may not be achieved in certain gasifiers and under many operating conditions, especially for gasifiers with relatively low operating temperatures [11, 19, 24]. Nevertheless, the models based on thermodynamic equilibrium have been the most widely used approach (see Fig. 2).

4.1.1. Stoichiometric vs Non-stoichiometric models

The most widely cited subcategories of equilibrium models are stoichiometric (S) models and nonstoichiometric (NS) models. This review, and a complimentary more detailed theoretical analysis of the S vs NS method elsewhere [102], indicates that approximately 72.5% of equilibrium simulations in the literature to date use the NS method, and the remaining 27.5% use the S method.

However, as rigorously shown elsewhere [102], S and NS models yield identical predictions in virtually all practical biomass gasification scenarios. Hence, the other categorization introduced in this work, namely between Eq-single (Eq-sing) and Eq-separate (Eq-sep) models is more significant. The model choice between an Eq-sing or an Eq-sep typically does significantly change the yield and product composition predicted by the model. Given these facts perhaps too much attention has been given in previous reviews, and studies, to a model choice (S vs NS) that does not matter in terms of the model prediction (i.e. two different computational strategies to get the same result). The reader will find that a majority of the published equilibrium studies listed in this review do discuss, typically in their introduction, the motivation for choosing either the S or NS approach, but virtually none of these studies explicitly mention or motivate the consequential Eq-sing vs Eq-sep model choice they also did make.

In the stoichiometric case, the equilibrium of a preselected *set of reactions* are computed, while in the nonstoichiometric case, the equilibrium of a preselected set of chemical species are calculated. In both cases, thermodynamic property data—combined with either the assumption of ideality or a thermodynamic model (EOS + mixing rule or activity model) to account for non-ideality of the mixture—are used to compute the predicted equilibrium composition that will exit the gasifier.

The steps for the stoichiometric method are the following: 1) *Select the reactions* to be included in the simulation (in principle, the dominant reactions assumed sufficient to provide a useful estimate of the product gas compositions), 2) then calculate the equilibrium constants of these reactions at the reaction temperature, and 3), finally, compute the overall chemical equilibrium composition for a given feed composition (and pressure).

 The explicit steps for the nonstoichiometric method are as follows: 1) *Select all the species* to be included in the simulation (in principle, all the chemical species that the modeler deems might be in the gasifier effluent in non-negligible amounts) and 2) then compute the resulting minimum Gibbs energy distribution among these chemical species for a given feed composition (which can be specified simply as the elemental composition of the feed [24, 91]) at the reaction temperature and pressure.

The simplest implementation of both the stoichiometric and nonstoichiometric approaches is to compute only the gas-phase equilibrium. That is, in the simulation, one does not use the actual feed but rather an "effective feed" that consists of the actual feed minus the fuel (moles and mass of C) that will become a specified amount of ash and unreacted char. In this

approach, the amount of ash in the char is an experimentally derived input parameter of the simulation. Essentially, the key question answered by both S and NS simulations (of the simplest gas only kind) is how all the gaseous carbon, oxygen, and hydrogen that ends up in the gas phase is distributed among the (gaseous) product species at ideal equilibrium at the temperature specified (or achieved in adiabatic simulation).

At this point, a key question is the following: Which of the two methods will better predict the composition of gasifiers that conform to assumptions 1 to 3 (listed at the outset of this section)? Or, alternatively, will the two methods always predict the same identical equilibrium composition? It is interesting that the literature is split down the middle on these questions. About half the gasification modelling studies published to date argue that the stoichiometric and nonstoichiometric approaches "are essentially equivalent" [19, 102]. Conversely, about half the articles that address this topic indicate that the nonstoichiometric approach is more accurate [17, 23, 24, 102, 103]. Although not completely absent, the opinion that the stoichiometric method is more accurately predictive of reality is rare in gasification modelling (which is not necessarily the case for other reactive systems) [102]. So in summary, about half the researchers in the field predict that NS is better, and the rest predict NS and S is identical.

To clarify this situation, and the roughly even split in the literature as to whether these two approaches necessarily lead to identical results or not, we published [102] a mathematical proof that shows that for the gas phase equilibrium the exact solutions to the stoichiometric and nonstoichiometric models are identical. Hence, if a stable and consistent numerical algorithm is used the equilibrium predicted by both methods (S and NS) will be identical.

The choice between the stoichiometric or the nonstoichiometric method in modelling the basic gasification system is therefore purely a matter of expediency. These approaches are two different methods that converge to the exact some predicted composition. (The exception to this may be more complicated systems than those typically encountered in gasification modelling; systems where there is a subset of reactions that do approach equilibrium and a subset of reactions that do not and where this subset of non-equilibrium reactions limits the product yield.)

4.1.2. Eq-single vs Eq-separate models

In addition to stoichiometric or nonstoichiometric, equilibrium models can be classified as Eq-sep (e.g. [30, 35, 36, 48, 61, 62, 71, 82, 89, 90]) or Eq-sing (e.g. [6, 10, 16, 32, 33, 39, 43, 45, 47, 53, 60, 69, 70, 88, 104-106]) approaches based on whether the char combustion is modeled as happening independently to reduction of the VM and un-combusted char or it all (combustion and reduction reactions) is subject to a single global equilibrium. Our survey indicates that about 75% of published biomass equilibrium simulations are of the Eq-sing type, with the remaining 25% of equilibrium simulations being of the Eq-sep type (see Fig. 5). Schematics of the 'process flow' within the algorithms for each type is shown in Figs. 7 and 8 respectively. It can be seen that the Eq-sep approach assumes equilibrium only between the

volatile components (produced in the pyrolysis step) and the char that is not combusted. Typically, either the fraction of tar combusted, or reduction zone temperature (which indirectly determines the amount of char that needs to be combusted to achieve the prescribed temperature) is a model input parameter. The Eq-sep approach thus models char combustion as occurring separately in a second heterogeneous reactor with heat flow from the second, exothermic 'combustion reactor' into the first gas-phase 'reactor' (even in single bed gasifiers where in reality there is only one 'reactor'). With the Eq-sing approach, the combustion and gasification of both the char and volatile gasses are modeled in a single reactor where a single overall heterogeneous equilibrium is assumed between all the components and all the reactions (combustion reactions and reduction reactions). Given that the choice between the stoichiometric and nonstoichiometric approach leads to identical solutions (see the discussion above [102]), but the Eq-sing and Eq-sep models typically will produce different final product compositions and yields, the choice between using an Eq-sing or Eq-sep model is more important. Yet notwithstanding this fact, this model choice is not discussed in any of the prior reviews on the modelling of gasification [17, 19-24] while the discussion of the S vs NS enjoy wide discussion in the literature and introductions of simulation studies.

In the remainder of this section the modelling steps, differences and relative merits of the Eq-sing versus Eq-sep models will be discussed. For both models the first step is modelling pyrolysis. The pyrolysis step is an extremely complex part of the gasification cycle, having a large number of chemical and physical phenomena occurring rapidly and simultaneously. Generally, when dried biomass is heated in across a temperature range of 200–500 °C during the pyrolysis step, the biomass decomposes into solid char and volatiles (tar and gases) as shown in Fig. 6. [25] For all model types the relative amounts of VM, char (also called fixed carbon) and ash (inert solid carbon) are typically computed based on empirically motivated input parameters. Within a stoichiometric model there needs to be a formula, or model, that determine not just the amount but also the molecular distribution of VM species produced by pyrolysis. The typical choice is to include H_2O, H_2, CO, CO_2, CH_4, N_2. Sometimes minor or trace elements like Cl_2, NH_3, H_2S and SO_2 etc. is also included if modelling the fate of the relevant elements and species are of interest. When using a non-stoichiometric model, the VM needs to be specified only in terms of the *amount* of every element present. (If the Gibbs minimization equilibrium reactor is operated isothermally then the equilibrium product distribution does change if one changes the distribution of atoms among the species present in the input stream [102]). Hence, within the computational algorithms or flow chart of a non-stoichiometric model the volatile output from the pyrolysis step is typically expressed simply as equivalent amounts of C, H_2, O_2, N_2, Cl_2, and S that is fed to the Gibbs minimization reactor. In both models char is also specified as a fraction of inert carbon produced in pyrolysis.
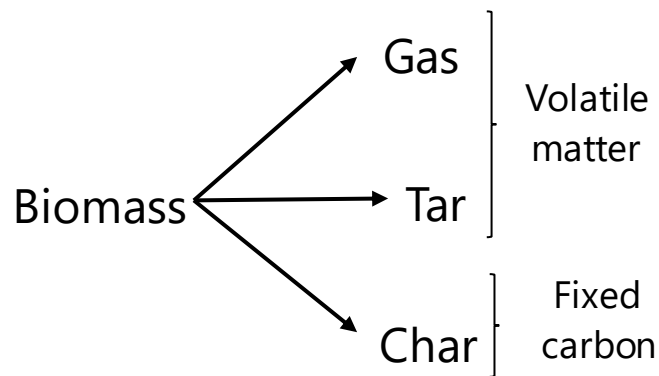
Fig. 6. Pyrolysis outputs

The pyrolysis outputs are not separated from each other in Eq-sing simulations. All three types of outputs in Fig. 6 enter the virtual gasifier (reactor in the model) together. The gasifier is a rigorous reactor for a multiphase chemical equilibrium to model or simulate the gasification of biomass based on the stoichiometric or nonstoichiometric approaches. A process flowchart of Eq-sing modelling is shown in Fig. 7.
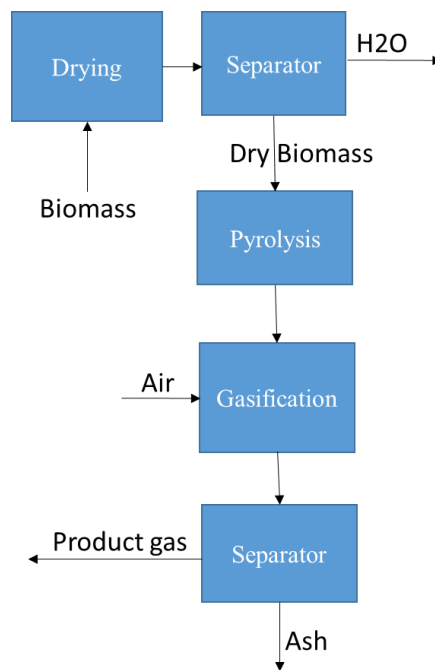

Fig. 7. Process flowchart of Eq-sing model

In the Eq-sep model, char is typically subdivided into the fraction of char that will be combusted and the remainder. This fraction can either be specified or internally calculated if the gasifier temperature is specified (since the combustion of char provides and thus determines the temperature of the gasifier/equilibrium reactor). Hence the fraction of char to be combusted is separated from the volatile materials and sent to the a virtual "char combustion reactor" together with air. Char combustion produces heat that supports most of

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endothermic gasification reactions, as well as the energy required by the drying and pyrolysis parts (i.e. any of these models include heat transfer from the combustion reactor to the pyrolysis and gasification reactors or computation blocks). The residual solid char (char not fed to the combustion reactor) is fed together the VM, remaining air (if any is not fed to the combustion reactor) and steam (in application with additional steam agent) to the relevant equilibrium reactor modelling gasification step (combustion and reduction zone).

The gasifier equilibrium is computed based on the equilibrium constants (stoichiometric method) or minimization of Gibbs free energy (nonstoichiometric approach), and the combustor is modeled based on combustion equations (Table 1). The combustion is typically assumed to be complete. Alternatively, an empirically motivated amount of unreacted oxygen can be assumed, or a separate heterogeneous equilibrium can be assumed in the combustor. Finally, in most simulations, all unreacted char and ash is separated from gas components of the product stream(s) using a virtual cyclone(s).

As can be seen in Fig. 8 the Eq-sep model was likely developed to model dual bed gasifiers, where combustion indeed physically happens in a separate chamber than reduction. But, subsequent researchers also started using the Eq-sep approach for single bed gasifiers (by following the purple as opposed to the orange route for the flue gas in Fig. 8) where combustion and reduction happens in the same reactor albeit, for the most part in different zones (or areas) of the reactor. The potential benefits and motivation for using a strategy that physically corresponds more closely to a dual bed configuration also for a 'single bed' reactor will become clearer in the next few paragraphs.
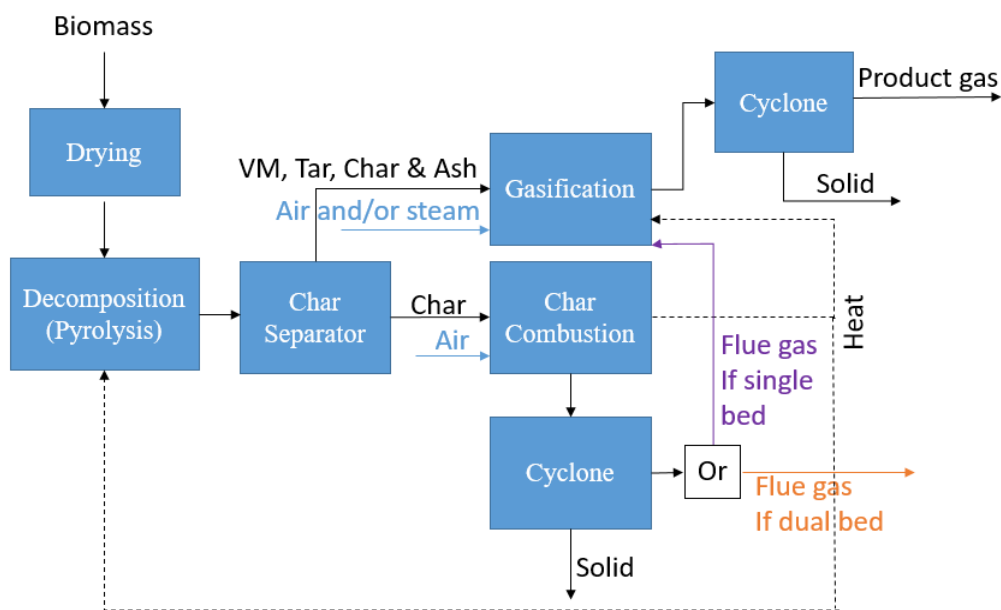

Fig. 8. Process flowchart of Eq-sep modelling

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The Eq-sing and Eq-sep models each have their own advantages and disadvantages. Eq-sing models are simpler in formulation however they frequently fail to yield satisfactory predictions of experimental gasification outputs. This failure is often attributed to the possibility that complete thermo-chemical equilibrium between all solid carbon (char atoms) and all gas-phase species may not be a realistic assumption for any given real-world gasifier. The notion of incomplete heterogeneous (solid-gas) equilibrium does explanation under prediction of equilibrium simulations of the amount of the residual char (or ash) produced in experiments. That is, for typical gasifiers, all gas-phase reactions and the gas-solid reactions most likely do not approach a single, perfectly global heterogeneous equilibrium where all solid phase atoms are accessible to all reactions. However, equally common deviations between equilibrium simulations (in particular ideal Eq-sing simulations) and experiments are the under prediction of the amount of CH_4 and/or CO_2 produced and an over prediction of the amount of CO and H_2 produced.

It is very common that all these deviations are compensated for by various quasi-empirical strategies. These include the pre-specification of amount of unreacted char (e.g. [107]), experimental adjustment or specification of some product components like methane (e.g. [74, 108, 109]), the use of an empirically adjusted (typically lower than actual measured) effective or quasi-equilibrium temperature rather than a single experimentally motivated lump average temperature (e.g. [110-112]) or empirical correction factors to the relevant equilibrium constants (e.g. [113]).

The Eq-sep method has the advantage that these empirically correlations and adjustments to ideal overall equilibrium can be more targeted and fine-tuned. Within the Eq-sep method the temperature of the combustion zone and reduction zone can be different, as in real gasifiers. Furthermore, heat flux between these can be adjusted to more accurately reflect imperfect heat transfer (which is real gasifiers is not instantaneous and infinite, i.e. there is losses and heat distribution to various gasifier zones is uniquely fractioned based on gasifier design and operating conditions). Note in Fig. 8 that it is important that the flue gas be sent along the right path that corresponds to the type of gasifier being modeled. In single bed gasifiers where the flue gas flow through the reduction zone the CO_2 (and/or H_2O) in the flue gas will shift or alter the WGS equilibrium (reaction R8 in table 1) in the reduction zone. To not include this effect will be physically inappropriate.

In summary, for a dual bed or circulating gasifier the Eq-sep model is really the only viable approach. For a single bed gasifier, the Eq-sing model has less adjustable parameters and is simpler. (It gives a pure theoretical equilibrium limit of the yield obtainable in an ideal single chamber gasifier where all homogenous and heterogeneous reactions approach a single global equilibrium.) However, the adjustable parameters (fractioning of heat flow etc.) in the Eq-sep approach do correspond to realistic features of actual gasifiers. Additionally, while combustion typically safely can be assumed to go to completion, some reduction reactions, in particular methane reforming, do not tend to reach full equilibrium in many experimental

tests. The Eq-sep model combined with the stoichiometric option provide the opportunity to exclude certain reactions from full equilibrium and model them separately, potentially in separate "virtual" reactors with heat exchange with other reactor blocks. This approach may, in some cases, more closely model real gasifiers where not all reactions operate close to equilibrium.

In summary, if the goal of an equilibrium simulation is to calculate purely the "thermodynamic limits", i.e. limiting yields obtainable under most ideal conditions – then the Eq-sing method achieves this goal with no assumptions or empirical fudge factors. However, if the goal of an equilibrium simulation is to predict the actual output of a non-ideal real gasifier, then the Eq-seperate method provides more opportunities for targeted introduction of empirical adjustments and factors that correct just the specific aspects of the real gasifier (e.g. reactions or zones) that do not approach ideal equilibrium.

4.1.3. How accurate can equilibrium models be?

In general, equilibrium models predict only the physically possible limits in the performance of a given gasifier at the given operating conditions. The observed product composition and syngas frequently fall short of the equilibrium's ideal. The most commonly reported and noteworthy deviations between ideal equilibrium predictions and experimental observations are, first, higher amounts of methane in the final syngas (compared with the equilibrium methane concentration) and, second, larger amounts of unreacted char in some cases [22, 107, 114, 115]. The unreacted char issue is best dealt with and avoided by only computing the equilibrium of the volatile gas-phase components rather than the complete heterogeneous equilibrium (Eq-gas approach) [89, 91, 102, 111, 114-116]. More accurate predictions can be obtained using empirical or experimental data (e.g., amount of residual char determined by experiments) to set the intimal conditions (atomic make-up and amount of volatile gasses generated). When it comes to higher methane yields than the equilibrium calculations predict, there is no easy work-around. It has been suggested that methane is released or formed during pyrolysis and that the methane gasification reaction rates simply are too slow in many gasifiers to fully approach equilibrium [22, 107, 115]. In such patently non-equilibrium conditions, in principle, only kinetic models could accurately predict the methane yields.

How large can the deviations between the observed gasifier yield and composition and the relevant thermodynamic equilibrium predictions get for typical practical applications? Loha et al., for example, found that in a steam-fed fluidized bed gasifier, the deviation of the amount of actual methane produced grows larger rather than smaller at higher temperatures [117, 118]. (This, of course, is exactly counterintuitive and widely quoted general rule of thumb that higher temperatures should be necessarily close rather than increase the gap between the equilibrium and measured composition.) For example, at 750 °C and a steam-to-biomass ratio of 0.6, the total percent of syngas composition measured to be methane by Loha et al. was 4.2 vol% compared with an equilibrium methane fraction that would be only

approximately 2 vol% [117]. Cases like this where the observed amount of methane is double, or even just more than the equilibrium amount, are fairly common [117-119]. Deviations between the equilibrium amounts and experimentally measured amounts of other syngas components (H_2, CO, CO_2) are invariably much less drastic (within 5 vol%) than the methane deviations that can occur in certain gasifiers [117-120].

4.2. Kinetic models

To precisely predict the non-equilibrium product distributions, kinetic modelling is required. Kinetic models can also predict gas composition and temperature profiles throughout the various gasifier zones as well as the evolution of these variables in time during non-steady-state operations and start-up. Because kinetic models have spatial resolution, they by necessity require detailed fluid dynamic modelling in addition to the kinetic model. In general, kinetic modelling can include not only the reaction kinetics and transport but could also include a model of the particle size distribution (and its evolution through the gasifier), micro-scale mass transport (e.g. diffusion into char particles) and mixing inside the gasifier. Notwithstanding this complexity that is potentially necessary to capture all the consequential physics.

Kinetic models can be very accurate and detailed, but this accuracy is difficult to achieve in practice since these models attempt to describe very complex phenomena, such as gas-solid-particulate fluid flows, gas–solid contacting process and microscopic evolution of particle distributions, which is hard to model reliably and also can be computationally intensive. The complexity and dimensions of the model are also increased with the desired model outputs, that is, with more detailed reaction kinetics and reactor hydrodynamics. However, because it has been frequently reported that the complex solid–fluid contact patterns of fluidized bed gasifiers may result in larger deviations from ideal equilibrium compositions (and ideal mixing), kinetic-hydrodynamic modelling is a particularly common approach chosen for modelling fluidized bed gasifiers, as argued by several authors [25, 28, 37, 38, 42, 51, 54, 56, 64]. The promise of potentially more accurate results motivates about 34% of the researchers who model gasification to employ simulations that model the kinetics of key reactions (see Fig. 5). As suggested, kinetic models can be divided into Kin-semi (e.g. [25, 37, 56]), Kin-total (e.g. [27, 28, 38, 52, 64, 72, 73, 81, 83, 85]), and Ki/Eq (CRF) (e.g. [31, 40-42, 58, 121]) approaches. Among articles with kinetic rate expressions in them our survey found that roughly 48% of biomass gasification studies published from 2000 – 2017 used a Kin-total model, roughly 24% used a Kin-semi model, and the remaining 28% used reversible rate expressions that limit to the thermodynamic equilibrium and empirical correction factors for the heterogeneous char reactions (the so-called CRF method).

The Kin-semi approach assumes local equilibrium for some reactions and/or gasifier zones but computes kinetically controlled concentrations and temperatures for other zones and/or reactions. Unlike the equilibrium models considered in section 4.1, within the simulation algorithm, the Kin-semi approach separates char from volatile matter (see Fig. 9A). Char—the

product of the drying and devolatilization step, is often modelled using an approximation that it consists of carbon only [27]. Like pyrolysis, char gasification is a complex process. It involves mass transfer (adsorption, diffusion, desorption, etc.), multiple chemical reactions, multiphase heat transfer, and so forth. The main chemical reactions of char gasification can be classified and subdivided into homogeneous and heterogeneous reactions (Table 1). Although there can be several variations in the way equilibrium and kinetic principles and calculations are combined, the most common implementation is the one shown in Fig. 9A (examples are [25, 51, 54, 59, 122]). In this, the most typical type of Kin-semi model, the volatile matter generated in the pyrolysis step first enters a volatile reactions module where a homogenous gas-phase equilibrium is computed by equilibrium constants or the minimization of Gibbs free energy. This equilibrated gas mixture is then fed, together with air/oxygen and/or steam and the solid char, into a kinetic module (which can be CSTR or a PFR) where reaction rate kinetics are used to determine the final composition from the reduction zone and where char gasification occurs. (Typical recent examples are [25, 123] . For alternative Kin-semi variations see, e.g., [56]).

Within Kin-total models, reaction rate kinetics simultaneously model both the volatile and char gasification reaction rates and local temperature and composition as the simulation code step through the reactor (which can be of any type, with the CSTR or PFR being the most common). Kin-semi models require less kinetic rate laws and parameters than Kin-total models. As a result, Kin-semi models can be more accurate than Kin-total models if the reactor conditions are such that the gas phase is close to the chemical equilibrium. Conversely, Kin-total models with reliable rate laws and hydrodynamic models are, in principle, the only option that could accurately describe non-ideal reactors and operating conditions.
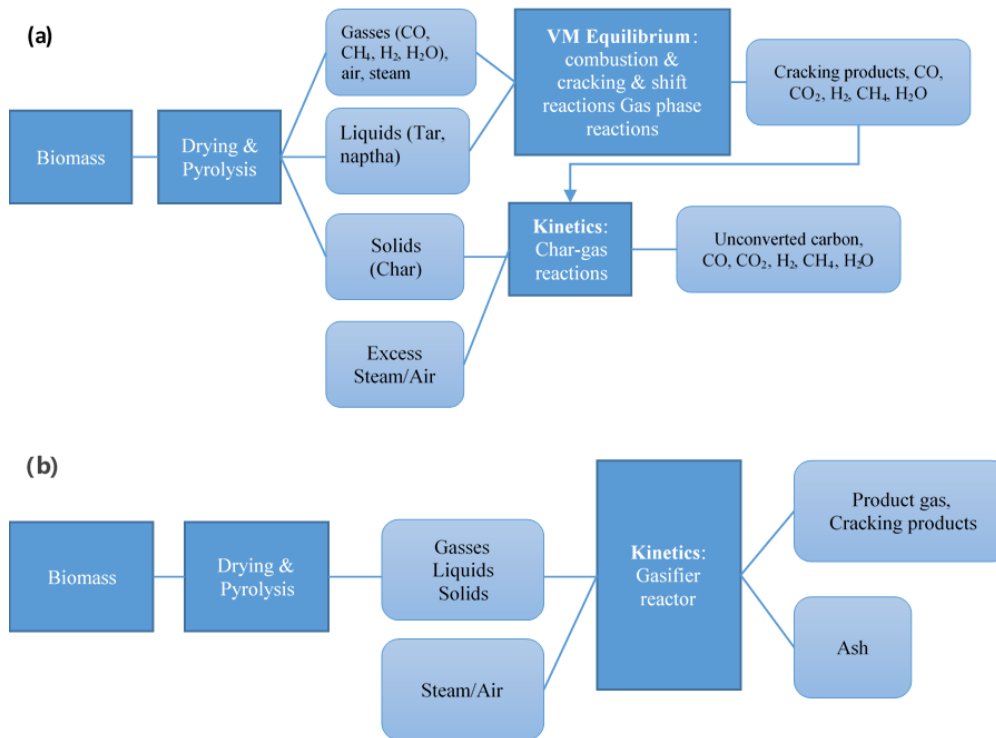
Fig. 9. Process flowcharts of (a) Kin-semi model, (b) Kin-total model

4.3. Kinetic/Equilibrium (CRF)

To complete this survey of modelling approaches one further modelling approach that does not fit neatly into either of the equilibrium categories or kinetic model categories considered this far. Unlike the Kin-semi method, the Ki-CRF approach models the reduction zone kinetically (i.e., all reactions and species concentrations are computed with a PFR-style rate law-based reactor model). However, the rate equations are typically formulated as a relatively simple Arrhenius type reversible that includes the equilibrium constants in the rate expressions to make all the equations thermodynamically consistent. Additionally, the pre-factors of these rate expressions for the reactions involving char are typically empirically adjusted by multiplying them with an adjustable parameter called the char reactivity factor (CRF). As such, this approach is a true hybrid of kinetic reactor modelling, thermodynamic equilibrium data, and empirical adjustments.

Ki-CRF models are designed to model gasifiers where the chemical composition of the product gas is not equal to the equilibrium composition, as is, for example, common with fluidized bed gasifiers. Ki-CRF models furthermore acknowledge the reality that truly reliable rate laws for especially heterogeneous char gasification reactions may not be available and that it may be more expeditious to utilize general thermodynamic equilibrium data and empirical CRFs in relatively simple rate expressions.

Generally, pyrolysis and cracking reactions are not considered in these models because the number of possible pyrolysis products with all the possible reactions and intermediate products would make the model very complex. Moreover, Ki-CRF models start at the top of

the reduction zone, so all the gasification calculations would be based on an empirical estimate of the initial feed into this section (assumption and empirically motivated estimates of the extent of combustion and pyrolysis). Hence, the accuracy of the model is limited by the availability of data on the initial conditions at the top of the reduction zone.

4.4. A survey of the models in the literature

A representative survey of studies modelling gasification is shown in Table A. 1 (in Appendix A Supplementary materials) [10, 16, 25, 27, 28, 30-43, 45, 47-49, 51-53, 55-57, 60-62, 64, 66, 67, 69-73, 81-83, 85, 88-90, 104, 105, 121, 124, 125]. The table can be consulted to quickly identify works relevant to certain types of gasifiers, feedstock, agents, and operating regimes or, conversely, to see how widely a given modelling approach has been applied across these applications (or not). It is clear from Table A. 1 that the number of variables both in terms of the physical variations modeled (gasifier type, agent choice, and feedstock) and the modelling approaches used (Ki or Eq) are large enough that many combinations have been studied, yet some others have not. This section will discuss some conclusions drawn from the survey data regarding what application areas have been well studied in the literature and what gaps or under studied areas may exist.

The data indicate that roughly more than 50% of the published works to date model fixed-bed gasifiers of mostly the downdraft type (downdraft gasifiers make up around 85% of the cases simulated in these fixed-bed studies, that is, fixed-bed downdraft gasifiers currently are the most popular gasifier to simulate, representing roughly 42.5% of all published simulation studies). Furthermore, our survey shows that most of the downdraft modelling utilizes thermodynamic equilibrium calculations, with more than half of all downdraft studies (~55%) using the Eq-sing approach. Moreover, it can be seen that the simulated operating temperature, steam to biomass ratio, air to biomass ratio, and equivalence ratio for downdraft gasifiers are in the ranges of 673–1673 K, 0.05–0.55, 1.35–1.9, and 0.1–0.9, respectively.

In addition, more than 80% of the downdraft models were used to simulate one or more species of untreated or pure wood (most typically in wood chip form) with air and steam as the gasification medium. In our survey, just Barman et. al [32] developed a model to simulate the gasification of treated wood with a downdraft gasifier. Barman et. al.'s [32] model is designed to simulate a fixed-bed downdraft gasifier. It is proposed that tar formation can be more significant when gasifying treated wood compared with clean wood. Barman et al. [32], however, also argued that the complexity of tar formation prohibits the predictive modelling of tar; hence, they instead simply used experimentally reported tar yields as fixed a priori *input* parameters in their simulation work (i.e., the simulations predict just the final distribution/yield of H_2, CO, CO_2, CH_4, and H_2O). Barman et al. [32] reported that their model predictions show fairly good agreement with results from prior models and various experimental investigations published by others. Following this validation, they used their

model to predict the optimum operating gasification temperature for straw, treated wood, and untreated wood.

Table A. 1 shows that around 40% of the published models are designed to model fluidized bed gasifiers. Circulating, bubbling, and entrained gasifiers all are represented in the models, with the most common subclass of kinetic model used being the Kin-semi approach. Moreover, the data show that when it comes to fluidized bed gasifiers, the following ranges of operating parameters have been of interest and hence have been simulated to date: temperatures of 600–1600 K, steam-to-biomass ratio (S/B) of 0–5, air to biomass ratio (A/B) of 1.25–5, and equivalence ratios (ER) of 0.29–0.38.

4.5. Tar modelling

It is worth considering the thoughts of alternative fuel and biomass gasification pioneer Thomas Reed [98], as follows:

"While a great deal of time and money has been spent on biomass gasification in the last two decades, there are very few truly commercial gasifiers, operating without government support or subsidies, day in, day out, generating useful gas from biomass. The typical project starts with new ideas, announcements at meetings, construction of the new gasifier. Then it is found that the gas contains 0.1-10% 'tars.' The rest of the time and money is spent trying to solve this problem. Most of the gasifier projects then quietly disappear. In some cases the cost of cleaning up the experimental site exceeds the cost of the project! Thus 'tars' can be considered the Achilles heel of biomass gasification. (In the gasification of coal, a more mature technology, the 'tars' (benzene, toluene, xylene, coal tar) are useful fuels and chemicals. The oxygenated 'tars' from biomass have only minor use. With current environmental and health concerns, we can no longer afford to relegate 'tars' to the nearest dump or stream."

Indeed, tar may be the single most important impediment to the practical implementation of biomass and organic waste gasification [7, 9, 98, 126] and a significant factor in environmental pollution from gasification [127, 128]. Tar has not only been neglected relative to other performance metrics in research studies, but perhaps also in the simulation sphere. All the articles included (see section 2) in our representative review suggest that just under 12% of all biomass gasification studies published from 2000 – 2017 include any tar modelling whatsoever. This section provides a brief overview of tar modelling approaches published to date.

The products of biomass gasification are of three types: gases, condensable tars, and solids (char and ash). By definition, tars are any condensable (mostly organic) compounds in the gasifier product stream [98]. Tar is generated predominantly during pyrolysis [97]. The subsequent fate of pyrolysis tar is then either to be cracked and gasified (reduced), combusted or it may persist (including transformation or "maturing" to higher molecular weight PAHs or soot) through combustion and reduction zones, in which case the residual tar either exists with the product gas or condenses and is deposited on downstream components [97, 98, 128]. The "stickiness" of tar condensate makes managing tar in downstream equipment an important practical challenge. For all these reasons, the modelling of tar

formation and persistence in high tar-producing applications such as biomass, municipal waste, or plastic gasification is of growing interest [9, 20, 25, 27, 125, 129]. However, the precise chemical composition of tar can be complex—Milne's lists of components contains 69 primary, 87 secondary, and 36 tertiary species, with the caveat that this list is partial and that "literally hundreds of other compounds have been identified in pyrolysis" [98]. Given that tar consists of a complex mixture that varies greatly depending on the process' operating conditions, feed, and gasifier type [20, 98], it should be no surprise that the precise chemical description of tar in all models invariably is and needs to be simplified, one with no simple and preferred one-size-fits-all formula [20]. Table A. 2 (in Appendix A Supplementary materials) provides an overview of the tar modelling choices made to date.

From Table A. 2, the chemical representation of tar currently is done with very simple models consisting frequently of only one—and at the most four—representative model compound. The estimation of tar yield is a difficult task using a thermodynamic equilibrium model because tar is typically a non-equilibrium product. Therefore, the predictions of tar yield in equilibrium models are mostly empirically fixed independently of the gasifier operating conditions, in accordance with other literature models. Moreover, in equilibrium models, tar is set as an inert component in the gasifier reactor; hence, tar cracking and tar reduction models are not possible. However, in kinetics models, tar decomposition has been mainly modeled because of cracking and steam and dry reforming reactions, as shown in Table A. 2.

5. Conclusion

A new classification of the most important gasification modelling approaches was presented, and the representative statistics of the frequency of their use was collected. Although the most appropriate choice of model depends on factors such as the goals of the simulation, the type of gasifier, feedstock, and operational parameters several general observations can be made.

For modelling downdraft gasification in particular, equilibrium models are typically a good starting point. Downdraft gasifiers frequently operate not too far from equilibrium because of their relatively simple geometry (and hence simpler hydrodynamics) and because of the relatively high operating temperature they typically employ. Furthermore, in downdraft gasifiers, both pyrolysis and gasification products are forced through the oxidation zone so that equilibrium is obtained after a brief time period [19]. It also can be observed from Table A. 1 that more than 65% of downdraft models employ the Eq-sing approach. Eq-sep models introduce somewhat more complexity and abstraction in formulation, but their predictions can be more accurate compared with Eq-sing models, as shown by the studies surveyed here. Moreover, Eq-sep models allow the researcher to assess in greater detail the impact of additional design features, such as the degree and location of combustion, heat transfer and loss from and between gasifier zones, and the effect of heat recovery from flue gas.

Even for the research that does embark on the more complex task of formulating a kinetic model, it still may be advisable to also run an equilibrium model of the same application. In

gasification, equilibrium can play the same role as in any other chemical system, namely revealing the thermodynamic limits of operation and how these limits depend on operating parameters and inputs (e.g., heat recovery, equivalence ratio, biomass moisture content, and steam injection). A drawback in using equilibrium modelling only is its inability to evaluate the impact of hydrodynamic parameters on gasification. If the goal is to optimize or understand the effect of parameters such as particle size distributions, feed density, and reactivity on the outlet gas composition, carbon conversion, and system performance, then a kinetic model would be required. However, the kinetic models generally contain kinetic and transport parameters that are hard to come by. Even if these parameters are measured, the resulting model will to some degree be limited to the specific gasifier type and design, feedstock, agent, and operating range combination for which the rate expression form and parameter values are valid.

In section 4.5 approximation methods used for tar modelling were surveyed. Tar modelling is likely to become one of the most active areas of research because of the central importance of tar avoidance for developing practically feasible and environmentally responsible biomass and waste (including plastics) gasification technology. Developing modelling approaches that can adequately provide scientific insight and/or practical operator guidance on how to manage tar formation is perhaps the most urgent challenge to be taken up by the biomass gasification modelling community.

Acknowledgements

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