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Improving the prediction of methane production and representation of rumen fermentation for finishing beef cattle within a mechanistic model

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Ellis, J. L., Dijkstra, J., Bannink, A., Kebreab, E., Archibeque, S., Benchaar, C., Beauchemin, K. A., Nkrumah, J. D. and France, J. 2014. **Improving the prediction of methane production and representation of rumen fermentation for finishing beef cattle within a mechanistic model**. Can. J. Anim. Sci. **94**: 509–524. The purpose of this study was to evaluate prediction of methane emissions from finishing beef cattle using an extant mechanistic model with pH-independent or pH-dependent volatile fatty acid (VFA) stoichiometries, a recent stoichiometry adjustment for the use of monensin, and adaptation of the underlying model structure, to see if prediction improvements could be made for beef cattle. The database used for independent evaluation of methane predictions consisted of 74 animal means from six studies. For the ''Bannink'' stoichiometries, pH-dependence of stoichiometry improved the root mean square prediction error (RMSPE) statistic (38.8 to 36.6%) but the concordance correlation coefficient (CCC) statistic was reduced (0.509 to 0.469). Inclusion of monensin in the stoichiometry improved both pH-independent and pH-dependent predictions. For the ''Murphy'' stoichiometries, pH-dependence worsened the RMSPE (31.2 to 33.7%) as well as the CCC (0.611 to 0.465) statistic. Inclusion of monensin in the stoichiometry improved predictions with the pH-independent but not with the pH-dependent stoichiometry. Results indicate that although improvements have been made to the mechanistic model, further improvement in the representation of VFA stoichiometry, and likely the representation and prediction of pH and neutral detergent fiber digestibility, are required for more accurate prediction of methane emissions for finishing beef cattle. However, inclusion of an adjustment for monensin feeding generally lead to improved methane predictions.

Key words: Finishing cattle, mechanistic modelling, methane, monensin, volatile fatty acid, stoichiometry

Ellis, J. L., Dijkstra, J., Bannink, A., Kebreab, E., Archibeque, S., Benchaar, C., Beauchemin, K. A., Nkrumah, J. D. et France, J. 2014. **Améliorer la prévision de la production de méthane et représentation de la fermentation dans le rumen chez les bovins de boucherie en phase de finition selon un modèle mécaniste**. Can. J. Anim. Sci. **94**: 509–524. Le but de cette étude était d'évaluer la prévision des émissions de méthane chez les bovins de boucherie en phase de finition au moyen d'un modèle mécaniste existant avec stoechiométries d'acides gras volatils dépendantes ou non du pH, un ajustement stoechiométrique récent pour l'ajout du monensin alimentaire, ainsi que l'adaptation de la structure de base du modèle, pour voir s'il est possible d'améliorer les prévisions chez les bovins de boucherie. La base de données utilisée pour l'évaluation indépendante des prévisions de méthane comprenait les moyennes de 74 animaux provenant de 6 études. Pour les stoechiométries « Bannink », la stoechiométrie dépendant du pH a amélioré la statistique RMSPE (38,8 à 36,6 %), mais la statistique CCC a été réduite (0,509 à 0,469). L'inclusion du monensin dans la stoechiométrie améliore les prévisions, qu'elles soient indépendantes du pH ou non. Pour les stoechiométries « Murphy », la dépendance au pH fait régresser la statistique RMSPE (31,2 à 33,7 %) en plus de la statistique CCC (0,611 à 0,465). L'inclusion du monensin dans la stoechiométrie améliore les prévisions dans la stoechiométrie indépendante du pH, mais non celle dépendante du pH. Les résultats indiquent que bien que des améliorations ont été apportées au modèle mécaniste, davantage d'améliorations dans la représentation de la stoechiométrie des acides gras volatils et probablement dans la représentation et la prévision du pH et de la digestibilité de la NDF sont nécessaires pour une prévision plus précise des émissions de méthane chez les bovins de boucherie en phase de finition. Par contre, l'inclusion d'un rajustement pour l'alimentation avec supplément de monensin offre généralement de meilleures prévisions des niveaux de méthane.

Mots clés: Bovins en stade de finition, modèle mécaniste, méthane, monensin, acides gras volatils, stoechiométrie

Abbreviations: **CCC**, concordance correlation coefficient; **CP**, crude protein; **DMI**, dry matter intake; **NDF**, neutral detergent fiber; **RMSPE**, root mean square prediction error; **RP**, roughage percent; **VFA**, volatile fatty acid

Central to accurate prediction of enteric methane (CH_4) production within dynamic mechanistic models of rumen fermentation and digestion is the need for accurate representation of rumen and hindgut fermentation as well as volatile fatty acid (VFA) stoichiometry (Bannink et al. 2008; Ellis et al. 2008). With fermentation, acetate and butyrate formation results in a net production of hydrogen, the main substrate for methanogens, and with propionate and valerate formation there is a net utilization of hydrogen. To date, inaccurate representation of VFA stoichiometry still seems to be a significant shortcoming in models of rumen function (Dijkstra et al. 2008; Morvay et al. 2011).

In an evaluation of the Dijkstra et al. (1992) rumen model [as modified by Mills et al. (2001) and Bannink et al. (2006)] performed by Kebreab et al. (2008), the model performed well on dairy cow data, but unsatisfactorily on beef cattle data in predicting CH_4 emissions. Results showed a tendency for the model to over-predict CH_4 production on the beef cattle data (μ value of -0.35), with a concordance correlation coefficient (CCC) of 0.160 and a root mean square prediction error (RMSPE) of 53.6% of the observed mean (Kebreab et al. 2008). Indeed, our initial evaluations revealed similar poor predictions on beef cattle data (Ellis et al. 2010).

The purpose of the present study, therefore, was to evaluate prediction of CH_4 emissions from finishing beef cattle using an extant model with two alternative pH-independent or pH-dependent VFA stoichiometries, with or without an adjustment for the use of monensin, and to perform an examination of the underlying model structure for suitability for finishing cattle, to see if prediction improvements could be made. As typical beef cattle finishing diets are higher in starch compared with typical dairy cow diets, and this is generally associated with low rumen pH, it was hypothesized that enteric CH_4 predictions for finishing cattle could be improved by including a pH-dependent VFA stoichiometry in the model. Other potential limitations of the extant model were examined including accounting for monensin feeding and by scaling the underlying model structure for application to finishing beef cattle fed high-grain diets.

MATERIALS AND METHODS

Simulation Model

The model evaluated in this study was the Dijkstra et al. (1992) rumen model as later modified by Mills et al. (2001) (collectively referred to here as the ''Dijkstra model'') to include prediction of CH_4 production and representation of hindgut fermentation and digestion, and more recently by Bannink et al. (2006 or 2008) to update the VFA stoichiometry. This mechanistic model is based on a series of dynamic, deterministic differential equations developed using dairy cow data. The model simulates microbial activity in the rumen and large intestine, production of fermentation end-products, digestion in the small intestine, absorption of nutrients and represents nitrogen, carbohydrate, lipid, microbial and VFA transactions. Required dietary chemical composition inputs to the model are neutral detergent fiber (NDF), crude protein (CP), starch, water-soluble carbohydrate, crude fat and ash content of the diet and also, if silage is present, acetate, propionate, butyrate, lactic acid and ammonia content. Dietary NDF, CP and starch are divided into rapidly fermented (CP and starch), potentially fermentable and nonfermentable fractions and a fractional degradation rate is applied to the potentially fermentable fraction, based on in situ data. In situ fractions and fractional degradation rates were obtained from the literature for identical ingredients evaluated on similar high-grain diets. The rapidly fermented fractions pass with the fluid phase and potentially fermentable/nonfermentable fractions pass with the solid phase in the model. For use with VFA stoichiometry, the model assumes that 0.55 of fiber entering the rumen is cellulose, and 0.305 of fiber entering the ileum is cellulose, although these fractions can be adjusted by the user.

VFA Stoichiometries

The CH_4 predictions made using several VFA stoichiometries (outlined in Table 1) within the Dijkstra model were tested. Murphy et al. (1982) developed a set of VFA stoichiometry parameters specific to high-forage and high-grain diets, including data from dairy cows, beef cattle and sheep [applied in the original rumen model of Dijkstra et al. (1992)] based on 108 diets (60 roughage and 48 concentrate diets). Subsequently, Argyle and

Table 1. Outline of VFA Stoichiometries

Stoichiometry Name	pH-dependent	Monensin-dependent	Reference
Bannink Line	No	No	Bannink et al. (2006)
	Yes	No	Bannink et al. (2008)
	No	Yes	Bannink et al. (2006) with Ellis et al. (2012)
	Yes	Yes	Bannink et al. (2008) with Ellis et al. (2012)
Murphy Line	No	No	Murphy et al. (1982)
	Yes	No	Murphy et al. (1982) with Argyle and Baldwin (1988)
	No	Yes	Murphy et al. (1982) with Ellis et al. (2012)
	Yes	Yes	Murphy et al. (1982) and Argyle and Baldwin (1988) with Ellis et al. (2012)

Baldwin (1988) developed an adjustment for starch and soluble carbohydrate VFA stoichiometries, dependent on pH. Combined, Murphy et al. (1982) and Argyle and Baldwin (1988) were used in the MOLLY model (Baldwin et al. 1987c; Baldwin 1995; MOLLY 2007) in the evaluation by Kebreab et al. (2008). This series of pH-independent and pH-dependent stoichiometries is referred to here as the "Murphy line" of stoichiometry.

The stoichiometry of Bannink et al. (2006) was also used in the evaluation of the Dijkstra model CH_4 predictions by Kebreab et al. (2008). This pH-independent stoichiometry describes the conversion of substrate (soluble carbohydrates, starch, hemicellulose, cellulose and protein) into VFA [a similar approach to Murphy et al. (1982)], and is based on an analysis of rumen digestion trials for 182 diets (96 roughage and 86 concentrate diets) in lactating dairy cows. Bannink et al. (2008) updated the VFA stoichiometry to include the effect of rumen pH on the fraction of the individual types of VFA (acetate, propionate and butyrate) produced from starch and soluble carbohydrate in roughage-rich or in concentrate-rich diets. The Bannink et al. (2008) stoichiometry is currently being used in the Dijkstra model as the Dutch Tier 3 approach to estimate CH_4 emissions in dairy cows in the Netherlands (Bannink et al. 2011). This series of pH-independent and pH-dependent stoichiometries is referred to here as the "Bannink line" of stoichiometry.

The effect of monensin feeding on VFA stoichiometry was also incorporated and evaluated. In a recent modelling exercise by Ellis et al. (2012), regressions were developed showing that the VFA profile of the rumen is significantly related to the dose of monensin received in high-grain diets fed to beef cattle. The relationships developed in Ellis et al. (2012) modify model-determined proportions of individual VFA (mol 100 mol^{-1} total VFA) according to monensin dose in the diet (mg $kg\ DM^{-1}$) as follows:

$$\begin{aligned}&\text{Acetate (mol 100 mol}^{-1}\text{ total VFA)}\\&\quad=\text{default acetate (mol 100 mol}^{-1}\text{ total VFA)}\\&\qquad\times(1.0-0.0634(\pm0.0323)\\&\qquad\times\text{monensin (mg kg}^{-1}\text{ DM)}/100)\end{aligned}\quad(1)$$

$$\begin{aligned}&\text{Propionate (mol 100 mol}^{-1}\text{ total VFA)}\\&\quad=\text{default propionate (mol 100 mol}^{-1}\text{ total VFA)}\\&\qquad\times(1.0+0.260(\pm0.0735)\\&\qquad\times\text{monensin (mg kg}^{-1}\text{ DM)}/100)\end{aligned}\quad(2)$$

$$\begin{aligned}&\text{Butyrate (mol 100 mol}^{-1}\text{ total VFA)}\\&\quad=\text{default butyrate (mol 100 mol}^{-1}\text{ total VFA)}\\&\qquad\times(1.0-0.335(\pm0.0916)\\&\qquad\times\text{monensin (mg kg}^{-1}\text{ DM)}/100)\end{aligned}\quad(3)$$

where the default VFA proportion (acetate, propionate or butyrate; mol 100 mol^{-1} total VFA) is the proportion of VFA determined as a result of the VFA stoichiometry represented in a given model, and the new calculated VFA proportion (mol 100 mol^{-1} total VFA) is adjusted for monensin dose via a proportional change, and VFA proportions are then adjusted to sum to 100% (Ellis et al. 2012). These equations were incorporated into the models of VFA stoichiometry for evaluation such that the impact of monensin in the diet on the VFA profile in the rumen could be quantified.

Thus, eight VFA stoichiometry scenarios are presented, representing the Dijkstra model CH_4 predictions after modification of the model (described below), with the VFA stoichiometry of (1) Bannink et al. (2006), (2) Bannink et al. (2006) with Ellis et al. (2012), (3) Bannink et al. (2008) and (4) Bannink et al. (2008) with Ellis et al. (2012), (5) Murphy et al. (1982), (6) Murphy et al. (1982) with Ellis et al. (2012), (7) Argyle and Baldwin (1988) and (8) Argyle and Baldwin (1988) with Ellis et al. (2012) (Table 1).

Methane Prediction

Total enteric CH_4 production is calculated from the rumen and hindgut hydrogen balance sub-models according to the model presented in Mills et al. (2001). This hydrogen balance sub-model is a development of the hydrogen model of Baldwin et al. (1987a, b, c), as also used in Benchaar et al. (1998). In this model, inputs to the H_2 pool (H_y; mol d^{-1}) include: (1) H_2 produced with acetate and butyrate (lipogenic VFA) during fermentation of carbohydrate and protein, and (2) H_2 produced as microbial populations utilize amino acids for growth. Outputs comprise: (1) H_2 utilized with fermentation and production of propionate and valerate (glucogenic VFA), (2) H_2 utilized for growth of microbes on non-protein nitrogen, and (3) H_2 utilized for biohydrogenation of ingested unsaturated fatty acids. In this representation H_y is a zero pool, meaning that net surplus of H_2 (H_2 produced minus H_2 utilized) is completely utilized for CH_4 production by methanogens. Methane production is hence estimated from the H_2 balance as CH_4 (MJ d^{-1}) $= (H_y/4) \times 0.883$, which assumes 4 moles H_2 are required to produce 1 mol of CH_4, and 0.883 is the heat of combustion of CH_4 in MJ mol^{-1} (Benchaar et al. 1998).

For external comparison, the empirical CH_4 prediction equations of IPCC Tier-2 [Intergovernmental Panel on Climate Change (IPCC) 2006] and equation 10b from Ellis et al. (2007), both developed specifically for beef cattle, were also evaluated. The IPCC Tier-2 approach for beef cattle assumes 3% of GE intake is converted into CH_4, and equation 10b from Ellis et al. (2007) assumes:

$$\begin{aligned}&\text{CH}_4\text{ (MJ d}^{-1})\\&\quad=-1.02(\pm1.86)+0.681(\pm0.139)\times\text{DMI (kg d}^{-1})\\&\qquad+0.0481(\pm0.0173)\times\text{roughage (\% dietary DM).}\end{aligned}$$

Evaluation Database

The database compiled for evaluation of CH_4 predictions consisted of data from beef cattle fed a high proportion ($>70\%$) of grain in the diet. The database included 74 animal $\times$ treatment means from Beauchemin and McGinn (2005, 2006), Nkrumah et al. (2006) and Archibeque et al. (2006, 2007a, b, c). The range of dietary variables is summarized in Table 2. Datasets included information on CH_4 production, body weight, chemical composition of the diet and any non-nutritional supplementation (e.g., monensin). As a full account of the dietary chemical composition and in situ degradation kinetics is required to run the Dijkstra model, missing values were estimated based on typical composition (Conrad et al. 1982; National Research Council 1996, 2000, 2001) and literature data. Silage VFA, lactic acid and ammonia content, as well as dietary lipid, water-soluble carbohydrate and ash content were generally estimated (although sometimes available). In situ degradation kinetic parameters for NDF, CP and starch were taken from the literature for similar feedstuffs used in similar basal diets. Dietary CP content was available for all treatments and NDF and starch were available for most. All data reported treatment with monensin (Elanco Animal Health, Greenfield, IN) except for Beauchemin and McGinn (2006). All studies measured CH_4 via indirect whole animal respiration calorimetry. For Archibeque et al. (2006, 2007a, b, c), observed CH_4 was measured for 6 h and scaled up to a 24-h basis. Unfortunately, not all studies in this database reported comprehensive information on variables such as diet digestibility (NDF, CP, starch), which are important indicators of underlying model performance. The studies that reported observed whole-tract or rumen values for these variables were used to evaluate digestibility predictions, in addition to the literature data of Gilbery et al. (2010), Yang et al. (2010) and Mezzomo et al. (2011).

Model Evaluation

The CH_4 and other output predictions were evaluated using two methods. First, mean square prediction error (MSPE), calculated as:

$$\text{MSPE} = \sum_{i=1}^{n}(O_i - P_i)^2/n \quad (4)$$

where n is the total number of observations, O_i is the observed value, and P_i is the predicted value. Square root of the MSPE, expressed as a percentage of the observed mean, gives an estimate of the overall prediction error. The RMSPE can be decomposed into error due to overall bias (ECT), error due to deviation of the regression slope from unity (ER) and error due to the disturbance (random error) (ED) (Bibby and Toutenburg 1977).

Second, concordance correlation coefficient analysis (CCC) was performed (Lin 1989), where CCC is calculated as:

$$\text{CCC} = P \times C_b \quad (5)$$

where P is the Pearson correlation coefficient and C_b is a bias correction factor. The P variable gives a measure of precision, while C_b is a measure of accuracy. Associated CCC variables (used in calculation of C_b) are v, which provides a measure of scale shift, and μ, which provides a measure of location shift. The v value indicates the change in standard deviation, if any, between predicted and observed values. A positive μ value indicates under-prediction, while a negative μ indicates over-prediction. These evaluation methods are summarized in Tedeschi et al. (2006).

Modifications to the Mechanistic Model

Upon examination of initial runs of the model using the CH_4 evaluation database, several issues were identified that required addressing before analysis of CH_4 predictions could proceed. The initial results revealed problems maintaining the fibrolytic microbial mass (Mc) pool

Table 2. Summary of the beef cattle CH_4 database

Variable	n	Mean	Median	SD	MIN[z]	MAX[y]
CH_4 (MJ d^{-1})	74	6.31	5.82	2.65	2.17	13.28
CH_4 (% GEI)	74	4.15	4.16	1.27	1.98	6.68
BW (kg)	74	428	435	65.2	303	592
DMI (kg d^{-1})	74	8.2	7.7	2.09	5.2	12.8
Forage (% of diet)	74	13	10	6.3	9	30
NDF (g kg DM^{-1})	74	181	182	20.5	147	215
WSC (g kg DM^{-1})[x]	74	33	31	10.5	22	54
Starch (g kg DM^{-1})	74	555	552	40.1	489	629
Protein (g kg DM^{-1})	74	133	134	13.5	115	160
Fat (g kg DM^{-1})	74	40	38	6.3	28	51
Monensin (mg kg DM^{-1})	74	17.4	17.6	8.75	0.0	33.0

[z]Minimum value.
[y]Maximum value.
[x]Water-soluble carbohydrate.

within the rumen on high-grain beef cattle diets (pool tended to zero for almost all data, and if no fibrolytic bacteria are present, fiber degradation is zero in the model), while at the same time unrealistically high fiber digestibility was predicted in the hindgut due to the resulting shift in site of fermentation away from the rumen. While a high-grain/low-pH rumen environment is not hospitable to Mc bacteria, in vivo observations do show that a population is still generally maintained in the rumen (Palmonari et al. 2010). Thus, the rumen model representation had to be improved for use with finishing beef cattle. The Dijkstra rumen and large intestine sub-models are identical in degradation and microbial growth equations, but differ in volume, passage rate, pH parameters and the presence of protozoa in the rumen. Besides too low rumen fiber degradation, initial results also revealed a seemingly high predicted rumen pH, despite the high starch content of the diet, which indicated further issues with the model.

This section describes the model developments that were required and are based on (1) new equations selected from the literature, (2) hypothesized mode of action and (3) regression analysis on independent data not used in subsequent model evaluation.

Protozoa Fractional Passage Rate

To assist survival of ruminal Mc bacteria, the representation of protozoal dynamics within the model required modification. Within the model, protozoa prey on Mc bacteria and thus their predicted mass impacts the survival of ruminal Mc. Of interest was the fractional passage rate of protozoa from the rumen. Not all studies support the premise that defaunation on high-concentrate diets is solely the result of low rumen pH (Slyter et al. 1970; Lyle et al. 1981; Towne et al. 1990). Instead, we propose that reduced protozoal numbers in the rumen with high-concentrate diets could also be partially the result of decreased bulk in the rumen and therefore decreased material on which protozoa can be selectively retained. Indeed, Hook et al. (2012) discussed observations on protozoal sequestration in relation to concentrate proportion of the diet, and since the proportion of protozoa in the liquid phase increases with higher concentrate levels, this will effectively increase the fractional passage rate of protozoa in the rumen. Based on this hypothesis, an equation was developed to predict protozoa fractional passage rate (k_{popa}; d^{-1}) based on solid passage rate and the roughage percent (RP;%) of the diet, such that when RP was less than 50% of the diet, k_{popa} was increased in relation to k_{sopa}:

$$k_{popa} = (1.0 - (0.5 + (\mathrm{RP} - 50)/100)) \times k_{sopa} \quad (6)$$

where k_{sopa} (d^{-1}) is the fractional solid passage rate. At RP greater than 50%, k_{popa} was $0.5 \times k_{sopa}$, as in the original model.

Ruminal Fractional Solid and Fluid Passage Rates

In the original model, linear solid and fluid fractional passage rate (k_p in general, k_{sopa}, k_{flpa}, specifically; h^{-1}) equations based on DMI were used for the rumen (Dijkstra et al. 1992), and these equations performed adequately for dairy cow data. However, 10 kg d^{-1} DMI for a 600-kg dairy cow is perceived differently in the digestive tract than it would for a 350-kg beef animal. For the dairy cow it could be considered a low intake, while for the beef animal it could be considered a high intake. Similarly, 10 kg d^{-1} of a 55% forage-based diet would have different effects on k_p than 10 kg d^{-1} of a 90% grain diet. As passage rate has a significant effect on microbial survival as well as diet digestibility [see Dijkstra et al. (1992) and Neal et al. (1992) for a discussion of model sensitivity], it is likely that not accounting for variation in k_p contributed to some of the issues identified in the original model outputs.

Thus, the k_{sopa} and k_{flpa} rate equations were replaced in the model with the recently developed k_{sopa} (combined roughage and concentrate) and k_{flpa} passage rate equations of Seo et al. (2006), which include parameters describing DMI, BW and RP to account for some of the normal variation not accounted for in the original fractional passage rate equations. These equations were based on a database containing data from all types of dairy and beef cattle diets, including diets up to 90% concentrate. The roughage and concentrate passage equations of Seo et al. (2006) were combined into a single solid passage rate equation based on RP, to conform to the structure of the existing model.

These changes to k_{sopa} and k_{flpa} predictions, combined with the modifications to k_{popa}, allowed a Mc population to be maintained in the rumen with simulations for most datasets.

Rumen Volume

Rumen volume (V_{ru}; L) affects everything expressed as a concentration within the model, including concentration of substrate and VFA (which are used to calculate pH), and thus model results are sensitive to V_{ru} [see Dijkstra et al. (1992) and Neal et al. (1992) for a discussion of model sensitivity]. The original model equation predicting V_{ru} contains the variable DMI (kg d^{-1}). While this equation has proved adequate for dairy cows, it is unsuitable for beef cattle diets where BW and RP of the diet differ substantially from those for average dairy cows. To address the scaling issue previously discussed, the original V_{ru} equation was scaled by BW with the equation:

$$V_{ru(\mathrm{BW\ adjusted})} = V_{ru(\mathrm{old})}/600 \times \mathrm{BW} \quad (7)$$

In addition to the BW adjustment, it was important to account for the RP of the diet, as an 80% roughage diet would have a much larger associated V_{ru} than an 80% concentrate diet. An equation was produced from the data of Colucci et al. (1990) to describe the average

across low and high DMI in order to predict the effect of RP on V_{ru}:

$$V_{ru(\text{final})} = [0.55(\pm 0.123) + 0.009(\pm 0.0021) \times \text{RP}] \times V_{ru(\text{BW adjusted})} \quad (8)$$

where $V_{ru(\text{BW adjusted})}$ is from Eq. 7. Since the average DMI of the CH_4 database was 19.1 ± 3.98 g kg BW^{-1} d^{-1} while the average DMI in Colucci et al. (1990) was 22.2 g kg^{-1} BW d^{-1}, it is possible that the adjustment for RP using Eq. 8 was severe for some data, causing an under-prediction of V_{ru} and higher than expected concentrations, which would drive faster rates of reactions within the model. Therefore, a "low-average" equation was developed from the Colucci et al. (1990) data (average between regressed "average" and "low" equations) ("low" equation not shown) aimed at an average DMI of 17.2 g kg BW^{-1} d^{-1}:

$$V_{ru(\text{final})} = [0.65(\pm 0.094) + 0.007(\pm 0.0016) \times \text{RP}] \times V_{ru(\text{BW adjusted})} \quad (9)$$

In the model, if DMI (g kg BW^{-1} d^{-1}) was less than 19.7, Eq. 9 was applied, and if DMI (g kg BW^{-1} d^{-1}) was greater than 19.7, Eq. 8 was applied. The switch point (19.7) is the halfway point between the average DMI values for each equation (17.2 and 22.2).

Prediction of V_{ru} with and without the above changes was evaluated using the following collection of papers where V_{ru}, DMI, BW and RP were available (and ranged from 17.2 to 104 L, 3.5 to 25.1 kg d^{-1}, 198 to 708 kg and 0.0 to 91.7%, respectively): McCollumn and Galyean (1983), Adams and Kartchner (1984), Goetsch and Owens (1985), Peters et al. (1990a, b), Johnson and Combs (1992), Murphy et al. (1994), Driedger and Loerch (1999), Rabelo et al. (2001), Tjardes et al. (2002), Koenig et al. (2003) and Reynolds et al. (2004). The observed V_{ru} mean for this database was 45.5 ± 3.49 L. Predicted values on this database with the original V_{ru} equation, with the BW adjusted equation (Eq. 7), with the average RP adjusted equation (Eq. 8) and with the low-average RP adjusted equation (Eq. 9), were 62.7, 51.1, 44.7 and 46.2 L, ± 1.74, 4.30, 5.03 and 4.93, respectively. Associated RMSPE values were 51.6, 45.3, 43.2 and 42.9%, respectively, random error consisted of 44.1, 58.7, 47.6 and 49.9% of this error, respectively, and the CCC statistics were 0.346, 0.625, 0.714 and 0.710, respectively. Results indicate improvements in V_{ru} prediction with the above adjustments, although applying the low-average equation if DMI (g kg BW^{-1} d^{-1}) was less than 19.7, only marginally changed predictions of V_{ru}.

The above series of model modifications allowed survival of the rumen microbial pools and satisfactory NDF, CP and starch digestibility predictions (evaluated below) within the rumen model. The hindgut section of the model posed similar challenges, and the following model modifications were required to allow survival of microbial pools and produce reasonable digestibility estimates in the hindgut.

Hindgut Fractional Solid and Fluid Passage Rates

The original Dijkstra hindgut fractional passage rate equation (k_{cfpa}; d^{-1}), which applies to passage of solids and fluids collectively, was based on DMI (kg d^{-1}) and suffered the same limitations as the ruminal fractional passage rates in not being able to account for extremes in BW or RP. Using the original k_{cfpa} equation resulted in the hindgut microbial pools tending towards zero. Unfortunately, hindgut passage rate in cattle has not been examined in as much detail as ruminal rates, and much less information is available on variation in k_{cfpa}. The original equation for hindgut k_{cfpa}, based on DMI as reported in Mills et al. (2001), was also scaled for differing BW in the model according to a similar procedure as for V_{ru} outlined above. This effectively increased k_{cfpa} in the model, which did not assist in predicting microbial survival. From the data of Colucci et al. (1990), k_{cfpa} with a 20% roughage diet was on average 0.86 times that with a 55% roughage diet. Regression of the influence of RP on k_{cfpa} on this data resulted in the following equation:

$$k_{cfpa(\text{new})} = k_{cfpa} \times [0.005(\pm 0.0022) \times \text{RP} + 0.68(\pm 0.126)] \quad (10)$$

where k_{cfpa} is the original hindgut fractional passage rate equation adjusted for BW, and $k_{cfpa(\text{new})}$ is the fractional passage rate further adjusted for RP. Passage of Ma and Mc bacteria in the hindgut (k_{cfmapa} and k_{cfmcpa}, respectively) were similarly modified for BW and RP. Tested back on the Colucci et al. (1990) data (and thus a non-independent evaluation for the RP adjusted equation), RMSPE values were 24.0, 24.9 and 19.8% for the original k_{cfpa} equation, the BW adjusted equation and the BW and RP adjusted equation, respectively, and CCC statistics were 0.571, 0.522 and 0.718, respectively. The RMSPE was mostly from deviation of the regression slope and from random sources for all three equations (46.0% ER and 50.1% ED for the BW and RP adjusted equation). On the CH_4 database the average unadjusted k_{cfpa} was 2.10 ± 0.077, for the BW adjusted k_{cfpa} 2.24 ± 0.084 and for the BW and RP adjusted k_{cfpa} 1.66 ± 0.102 d^{-1}.

Hindgut Volume

In the original model, hindgut volume (V_{hg}; L) was calculated as 9% of V_{ru}, and thus all of the above modifications to V_{ru} due to BW and RP carry through to V_{hg} prediction. However, the combined work of Goetsch and Owens (1986a, b) also suggests that V_{hg} (% of V_{ru}) varies directly with RP of the diet. Thus, the V_{hg} equation was amended, following regression on the Goetsch and Owens (1986a, b) data, to:

$$V_{hg}\ (\%\ V_{ru}) = [-0.18(\pm 0.078) \times \text{RP} + 19.2(\pm 4.56)] \quad (11)$$

such that as RP declines, V_{hg} is a higher proportion of the estimated V_{ru}. While this regression passes almost directly through the original model value of 9% at an RP value of 55% (typical dairy cow diet), caution should be used in applying the expression outside the range of data over which it was developed (RP range = 14–81%).

Hindgut Fiber Degradation Kinetic Parameters

The above improvements shifted ruminal fiber digestibility and pH to more expected levels, but whole tract fiber digestibility remained high, and initial results with test data suggested that the model continued to over-predict hindgut fiber digestibility. In a review of microbial inocula, Mould et al. (2005) suggested that differences exist in the kinetics of gas production rate in ruminal versus fecal bacteria. Mould et al. (2005) state that when compared with rumen fluid, fecal inocula show a similar pattern of starch fermentation but fiber degradation is reduced, and differences in fermentation patterns are evident. On average, maximum gas production rate in the fecal sample for three substrates evaluated was 39.5% lower than in the rumen sample.

The review by Mould et al. (2005) and the results of others (Hecker 1971; Aiple et al. 1992; Goncalves and Borba 1996; Nsahlai and Umunna 1996; Mauricio et al. 1997; El-Meadaway et al. 1998; Dhanoa et al. 2004) support the observation that when the same kinetic parameters are used to describe fiber fermentation in the hindgut as in the rumen section of the model, over-prediction of fiber digestibility in the hindgut may occur. Whether this is due to a lower maximum velocity or a higher affinity constant for fiber fermentation is unknown, but for purposes here, a reduction of 39.5% was placed on the maximum velocity parameter for fiber fermentation in the hindgut.

RESULTS AND DISCUSSION

Diet Digestibility Predictions

Predictions of NDF, CP and starch digestibilities were evaluated for the model post-modifications, as described above. It would not be appropriate to compare these to pre-modification values, as the model was not functioning properly using these data (e.g., microbial pools tending to zero). Evaluation of NDF, CP and starch digestibility predictions according to RMSPE and CCC analysis are presented in Table 3, and plots of observed versus predicted values are presented in Fig. 1. The CH_4 database did not collectively or consistently report NDF, CP and starch digestibility, but predictions were evaluated for the limited data that were available for each to give an idea of model performance. Predictions of CP and starch digestibility by the model showed low RMSPE values, with the largest portion of error coming from random sources, and reasonable CCC values. There was a slight tendency for CP digestibility to be under-predicted and for starch digestibility to be over-predicted (on average). The NDF digestibility predictions by the model were more variable, with a higher RMSPE and lower CCC statistic than obtained for CP and starch digestibility, and a tendency for the average to be over-predicted. Since the level of dietary NDF is much lower than that of starch, quantitatively, errors in NDF digestibility would have a smaller impact on the model results than errors in starch digestibility. The NDF digestibility was the most difficult component to predict accurately, reflecting the challenge of

Table 3. Diet digestibility and pH predictions by the model[z]

Variable	*n*	Observed mean[y]	Predicted mean[y]	RMSPE (%)[x]	ECT (%)[w]	ER (%)[v]	ED (%)[u]	CCC[t]	P[s]	C_b[r]	v[q]	μ[p]
Digestibility (%)												
NDF	28	53.7 (±11.6)	59.0 (±8.3)	25.0	15.9	15.3	68.8	0.220	0.264	0.830	1.39	−0.55
CP	70	70.0 (±3.0)	68.7 (±2.6)	3.3	32.0	1.3	66.7	0.696	0.779	0.893	1.15	0.47
Starch	20	92.9 (±1.9)	93.9 (±1.5)	1.6	41.6	8.4	50.0	0.669	0.818	0.824	1.28	−0.57
Ruminal pH	21	6.20 (±0.38)	5.91 (±0.20)	8.7	30.5	21.9	47.7	−0.079	−0.139	0.555	1.90	1.10

[z]Simulated after modifications to the basal model as described in the Materials and Methods section, where values presented are the average across all VFA stoichiometry scenarios (digestibility predictions with differing VFA stoichiometries varied slightly due to the effect of VFA profile on rumen pH and the subsequent effect of rumen pH on fermentation), and where the data used to evaluate NDF digestibility came from Beauchemin and McGinn (2005), Nkrumah et al. (2006), Yang et al. (2010), Mezzomo et al. (2011) and Gilbery et al. (2010), data used to evaluate CP digestibility came from Archibeque et al. (2006, 2007a, b, c), Beauchemin and McGinn (2005), Nkrumah et al. (2006), Yang et al. (2010), Mezzomo et al. (2011) and Gilbery et al. (2010), data used to evaluate starch digestibility came from Archibeque et al. (2006, 2007a, b, c) and Yang et al. (2010), and data used to evaluate pH came from Beauchemin and McGinn (2005, 2006), Yang et al. (2010), Mezzomo et al. (2011) and Gilbery et al. (2010).
[y]Where values are expressed as mean ± standard deviation.
[x]Root mean square prediction error (MJ d^{-1}), % of observed mean.
[w]Error due to bias, as a % of total MSPE.
[v]Error due to regression, as a % of total MSPE.
[u]Error due to disturbance, as a % of total MSPE.
[t]Condordance correlation coefficient, where CCC = $P \times C_b$.
[s]Pearson correlation coefficient.
[r]Bias correction factor.
[q]Scale shift.
[p]Location shift.

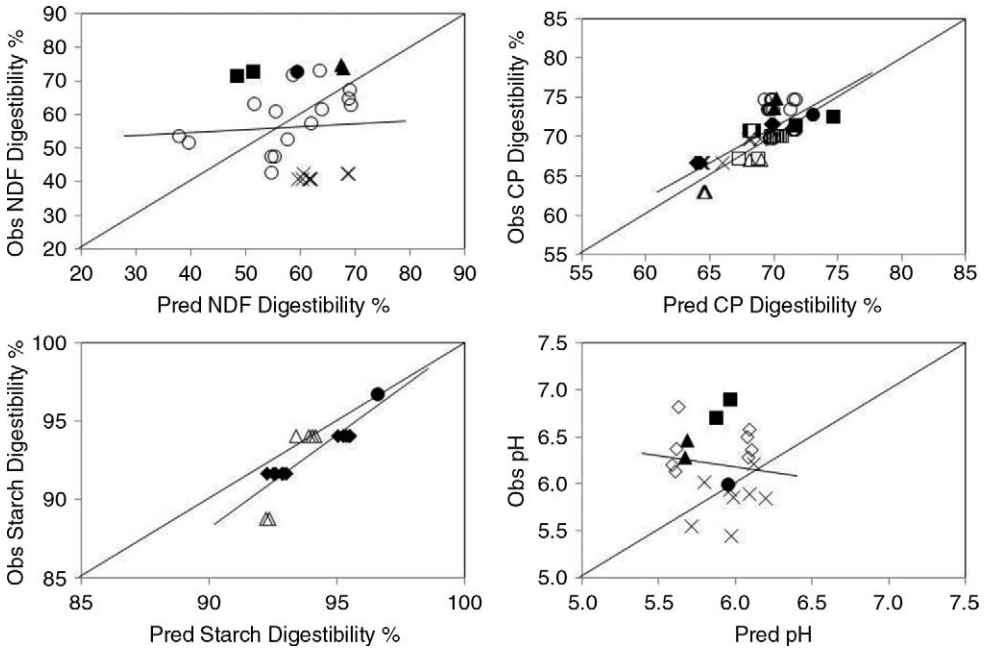

Fig. 1. Observed versus predicted NDF, CP, starch digestibility% and ruminal pH for the modified model, illustrated using the VFA stoichiometry of Bannink et al. (2008) with Ellis et al. (2012), and where the data used to evaluate NDF digestibility came from Beauchemin and McGinn (2005) (×), Nkrumah et al. (2006) (○), Yang et al. (2010) (●), Mezzomo et al. (2011) (■) and Gilbery et al. (2010) (▲), data used to evaluate CP digestibility came from Archibeque et al. (2006, 2007a, b, c) (◆, □, Δ), Beauchemin and McGinn (2005), Nkrumah et al. (2006), Yang et al. (2010), Mezzomo et al. (2011) and Gilbery et al. (2010), data used to evaluate starch digestibility came from Archibeque et al. (2006, 2007c) and Yang et al. (2010), and data used to evaluate ruminal pH came from Beauchemin and McGinn (2005, 2006) (×, ◇), Yang et al. (2010) (●), Mezzomo et al. (2011) (■) and Gilbery et al. (2010) (▲).

maintaining the slow growing Mc population in the rumen and hindgut against low pH and high fractional passage rates. In vivo, survival of a Mc population in the rumen is assisted by dynamic changes and fluctuations in pH throughout the day, spatially within the rumen, as well as through cross-feeding of cellodextrins (Dijkstra et al. 2012). This allows low NDF digestibilities to be maintained without complete extinction of the Mc bacteria population. In a rumen model assuming total mixing and run to steady state, these advantages cannot be simulated and balancing growth and retention of micro-organisms becomes challenging.

pH Predictions

Rumen pH was not reported in many of the studies in the CH_4/digestibility database (available $n = 21$). Evaluation of pH predictions on this limited data showed a tendency for pH to be under-predicted, and although the RMSPE was relatively low, the CCC statistic was quite poor (Table 3; Fig. 1). This slight under-prediction may have had a minor limiting effect on fiber fermentability in the rumen and contributed towards a lower Mc population than would have been observed with precise pH prediction.

The Dijkstra model bases rumen pH prediction on concentration of VFA in the rumen, but rumen pH is also influenced by buffers present in the diet, the cation exchange capacity of dietary cell walls and bicarbonate secretion through saliva production as influenced by effective dietary NDF content, or via bicarbonate dependent absorption of VFA [reviewed by Dijkstra et al. (2012)]. Mezzomo et al. (2011) suggested that high rumen pH values observed in their study, despite only 13% roughage in the diet, could be because of the use of sugar cane bagasse, which has high levels of effective fiber and stabilizes the rumen environment via increasing rumination and saliva production. Gilbery et al. (2010) used chopped alfalfa, whereas some other studies in the CH_4 database used ground alfalfa, which would be much lower in effective fiber. Beauchemin and McGinn (2005, 2006) and Yang et al. (2010) used corn and barley silage, though the chop length and effective fiber content were not reported. The Dijkstra model determines saliva production based on DMI and NDF in the diet, but saliva buffering is not currently incorporated into calculation of pH, nor are any of the other factors mentioned above simulated. It is possible, if saliva production or other factors buffering ruminal pH were incorporated into model pH calculations, that ruminal pH predictions for some of the database would become higher. However, modeling of rumen pH is complex and challenging. In addition, as discussed in the Materials and Methods section, prediction of pH via VFA concentration will also be sensitive to prediction of

V_{ru}, as anything driven by concentration is sensitive to volume. It is also possible that the equations developed for V_{ru} are not applicable to these data for some reason, but this is difficult to determine without observed V_{ru} values to compare against. An empirical representation of V_{ru} was taken for this exercise, which allowed consideration of the RP% of the diet DMI and BW, but other approaches such as that of Chilibroste et al. (2001) may be valid as well, where discontinuous feeding is represented and V_{ru} is described mechanistically over time based on the DM% of rumen contents. As discontinuous feeding pattern data were not available for the independent beef database, an empirical approach was logical, although further investigation of whether the Chilibroste et al. (2001) approach results in better predictions could be warranted.

Without pH values for the entire database it is difficult to conclude that prediction of pH is adequate or inadequate, but it is likely an area requiring further attention. Indeed, much emphasis has been placed on advancing measurements, understanding and modelling of rumen pH (Dijkstra et al. 2012).

Methane Predictions

Stoichiometry Selection

While this study considered the importance of rumen pH in CH_4 predictions for high-grain-fed beef cattle via the application and comparison of pH-independent and pH-dependent stoichiometries, other stoichiometric approaches also exist, which could have been considered but were excluded for a number of reasons. First, the Murphy and Bannink stoichiometry lines are the only ones available with a pH-dependent and pH-independent version. In view of the objectives of the present study, these were therefore of prime interest. Second, Alemu et al. (2011) recently performed a comparison between four stoichiometries, namely Murphy et al. (1982), Bannink et al. (2006), Sveinbjörnsson et al. (2006) and Nozière et al. (2010) for dairy cattle. Sveinbjörnsson et al. (2006) developed a VFA stoichiometry for the Nordic dairy cow model Karoline (Danfær et al. 2006). This stoichiometry is similar to Bannink et al. (2006), but with some dietary factors as additional explanatory variables, and it was developed on a database of Nordic dairy cow digestion trials. Nozière et al. (2010) took a different approach, and empirically derived relationships for total and individual VFA in the rumen based on dietary and digestibility variables including DMI, digestible NDF, digestible OM and ruminal starch digestibility. From the Alemu et al. (2011) evaluation, the Bannink et al. (2006) stoichiometry performed best (on average), followed by Nozière et al. (2010), and Sveinbjörnsson et al. (2006) performed worst. Thus, the Bannink et al. (2006) stoichiometry was deemed a good starting point for the current project. In addition, it presented the ability to compare against a similar but pH-dependent stoichiometry (Bannink et al. 2008).

In the paper by Kebreab et al. (2008), the Dijkstra model, with the VFA stoichiometry of Bannink et al. (2006), performed least well in terms of CH_4 predictions for beef cattle data when compared against MOLLY [which included the stoichiometry of Argyle and Baldwin (1988), Baldwin (1995), MOLLY (2007)], Moe and Tyrrell (1979) and IPCC (2006) Tier 2 predictions, despite performing best for the dairy cow data. Since finishing beef cattle are typically fed a high-grain diet, resulting in low rumen pH, it was hypothesized that the pH-dependent VFA stoichiometry of Bannink et al. (2008) would improve CH_4 predictions by the Dijkstra model for this type of data. Similarly, that the pH-dependent VFA stoichiometry of Argyle and Baldwin (1988) compared with the pH-independent stroichiometry of Murphy et al. (1982) would improve CH_4 predictions. Moreover, we hypothesized that accounting for monensin use in the diet might improve predictions further.

Model Evaluation

Results of MSPE and CCC analysis are presented in Table 4 for the mechanistic model with varying VFA stoichiometries, as well as the results for the empirical equations considered. Observed versus predicted plots are presented in Figs. 2 and 3. Overall, the stoichiometry of Murphy et al. (1982) with the monensin adjustment of Ellis et al. (2012) resulted in the best RMSPE and CCC prediction statistics (Table 4). Results show that the Bannink et al. (2006, 2008) stoichiometries had a tendency to over-predict CH_4 emissions (MJ d^{-1}) using the beef cattle database (Table 4, Fig. 2a), while the stoichiometry of Argyle and Baldwin (1988) used in MOLLY tended to under-predict CH_4 emissions. The lower CH_4 predictions on average for the Murphy line of stoichiometry compared to the Bannink line could be the result of inclusion of data from beef cattle fed high-grain diets (where there is a trend for high propionate levels and lower CH_4 values) in the developmental database, whereas the Bannink line of stoichiometry was developed on, and intended solely for, lactating dairy cows. The high propionate values seen with high-grain-fed beef cattle simply did not occur in the database used to develop the Bannink et al. (2006, 2008) stoichiometries. It should, however, be noted that on average the Dijkstra model also slightly over-predicted NDF digestibility, albeit on a limited test database. If NDF digestibility has a tendency to be over-predicted by the basal model, then it is possible this can account for some of the over-prediction by the Bannink line of stoichiometry simulations and that this is not due solely to the stoichiometry. Similarly, this may make the Murphy et al. (1982) predictions more accurate, where CH_4 is currently slightly over-predicted on average, but may worsen Argyle and Baldwin (1988) predictions where CH_4 is already under-predicted. Evaluation of diet digestibility predictions by the mechanistic models was not performed by Kebreab et al.

Table 4. Summary of methane (CH_4)[z] prediction statistics for the revised Dijkstra model using various VFA stoichiometries

VFA Stoichiometry	Predicted CH_4 mean (MJ d^{-1})[z]	RMSPE (%)[y]	ECT (%)[x]	ER (%)[w]	ED (%)[v]	CCC[u]	P[t]	C_b[s]	v[r]	μ[q]
Bannink et al. (2006)	7.84 (±1.70)	38.8	38.7	0.3	60.9	0.509	0.692	0.736	1.56	−0.72
Bannink et al. (2006) with Ellis et al. (2012)	7.58 (±1.67)	35.9	31.2	0.8	67.9	0.550	0.709	0.776	1.58	−0.60
Bannink et al. (2008)	7.36 (±1.40)	36.6	20.4	1.5	78.1	0.469	0.636	0.737	1.89	−0.54
Bannink et al. (2008) with Ellis et al. (2012)	7.16 (±1.33)	34.7	15.1	4.1	80.8	0.495	0.668	0.740	1.99	−0.45
Murphy et al. (1982)	6.82 (±1.64)	31.2	6.7	1.2	92.2	0.611	0.700	0.872	1.61	−0.24
Murphy et al. (1982) with Ellis et al. (2012)	6.56 (±1.57)	29.8	1.7	3.3	95.0	0.630	0.723	0.872	1.68	−0.12
Argyle and Baldwin (1988)	5.99 (±1.16)	33.7	2.4	6.5	91.1	0.465	0.642	0.724	2.29	0.19
Argyle and Baldwin (1988) with Ellis et al. (2012)	5.68 (±1.07)	34.8	8.4	9.6	82.0	0.438	0.661	0.663	2.47	0.38
IPCC (2006) Tier-2 for feedlot beef cattle[p]	4.63 (±1.15)	43.1	38.3	3.2	58.5	0.336	0.618	0.544	2.31	0.97
Ellis et al. (2007) Eq. 10b[o]	5.22 (±1.51)	39.7	18.9	0.2	80.9	0.401	0.526	0.763	1.76	0.55

[z]Where the observed mean is 6.31 (±2.65) MJ d^{-1} and values are expressed as mean±SD, $n = 74$.
[y]Root mean square prediction error (MJ d^{-1}), % of observed mean.
[x]Error due to bias, as a % of total MSPE.
[w]Error due to regression, as a % of total MSPE.
[v]Error due to disturbance, as a % of total MSPE.
[u]Condordance correlation coefficient, where $CCC = P \times C_b$.
[t]Pearson correlation coefficient.
[s]Bias correction factor.
[r]Scale shift.
[q]Location shift.
[p]Where CH_4 (MJ d^{-1}) = 0.03 × GE intake (MJ d^{-1}).
[o]Where CH_4 (MJ d^{-1}) = −1.02(±1.86)+0.681(±0.139) × DMI (kg d^{-1})+0.0481(±0.0173) × Roughage (%).

(2008), and therefore it is not known whether errors in CH_4 prediction reported there are due to prediction of the extent of fermentation or due to representation of VFA stoichiometry. In the evaluation by Kebreab et al. (2008), the MOLLY model (with Argyle and Baldwin stoichiometry) as a whole did have a tendency to under-predict CH_4 emissions, as indicated by a μ value of 0.08, which is in agreement with the current results.

In Kebreab et al. (2008), the Dijkstra model with Bannink et al. (2006) VFA stoichiometry resulted in a RMSPE of 53.6% and a CCC of 0.160. As the current database includes additional data compared to the beef cattle database of Kebreab et al. (2008), a direct comparison between studies cannot be made. However, the result in Table 4 for the Bannink et al. (2006) VFA stoichiometry is the closest direct comparison to the results obtained by Kebreab et al. (2008) for the Dijkstra model. With the current database, the same stoichiometry resulted in a RMSPE of 38.8% and a CCC of 0.509. Some of the improvement could be due to the larger database, but also due to the model developments undertaken pre-analysis as described above. The evaluation of the MOLLY model by Kebreab et al. (2008) is not directly comparable to the use of MOLLY stoichiometry in the current study, but in the former the RMSPE was 22.3% and CCC was 0.455, compared with 33.7% and 0.465 in the current study.

One hypothesis of the current paper was that CH_4 predictions would improve with application of pH-dependent stoichiometry because of the tendency for low pH values in high-grain-fed finishing cattle. Such low pH values are not foreign to dairy cows, where high rates of DMI can cause a high intake of non-structural carbohydrate and subsequently low rumen pH. In the current evaluation, in only one instance did the pH-dependent stoichiometry perform better than the pH-independent stoichiometry (Table 4). Switching from Bannink et al. (2006) to Bannink et al. (2008), the RMSPE improved, while in all other comparisons RMSPE and CCC were worse with the pH-dependent stoichiometry. Also, regardless of which stoichiometry line is examined, there is a loss of predicted CH_4 variation (larger v statistic, the ratio of observed to predicted SD, Table 4) with the pH-dependent stoichiometries. This may indicate a lack of variation in predicted pH (see Fig. 1), leading to poorer CH_4 predictions. Given the limitations to pH prediction discussed above, it is difficult to separate how much of the CH_4 prediction error is due to pH prediction versus the VFA stoichiometry. Either way, it is clear that both are still areas within mechanistic digestion models that require attention and further work.

In comparison, the IPCC (2006) Tier-2 and Ellis et al. (2007) 10b equations, developed for beef cattle fed high-grain diets, tended to under-predict CH_4 emissions on this database, and also had considerably higher RMSPE and lower CCC values than any of the VFA stoichiometry approaches. Although the prediction accuracy of the Bannink and Murphy line requires improvement, the accuracy of these approaches is higher than that of the IPCC Tier-2 and Ellis et al. (2007) equations.

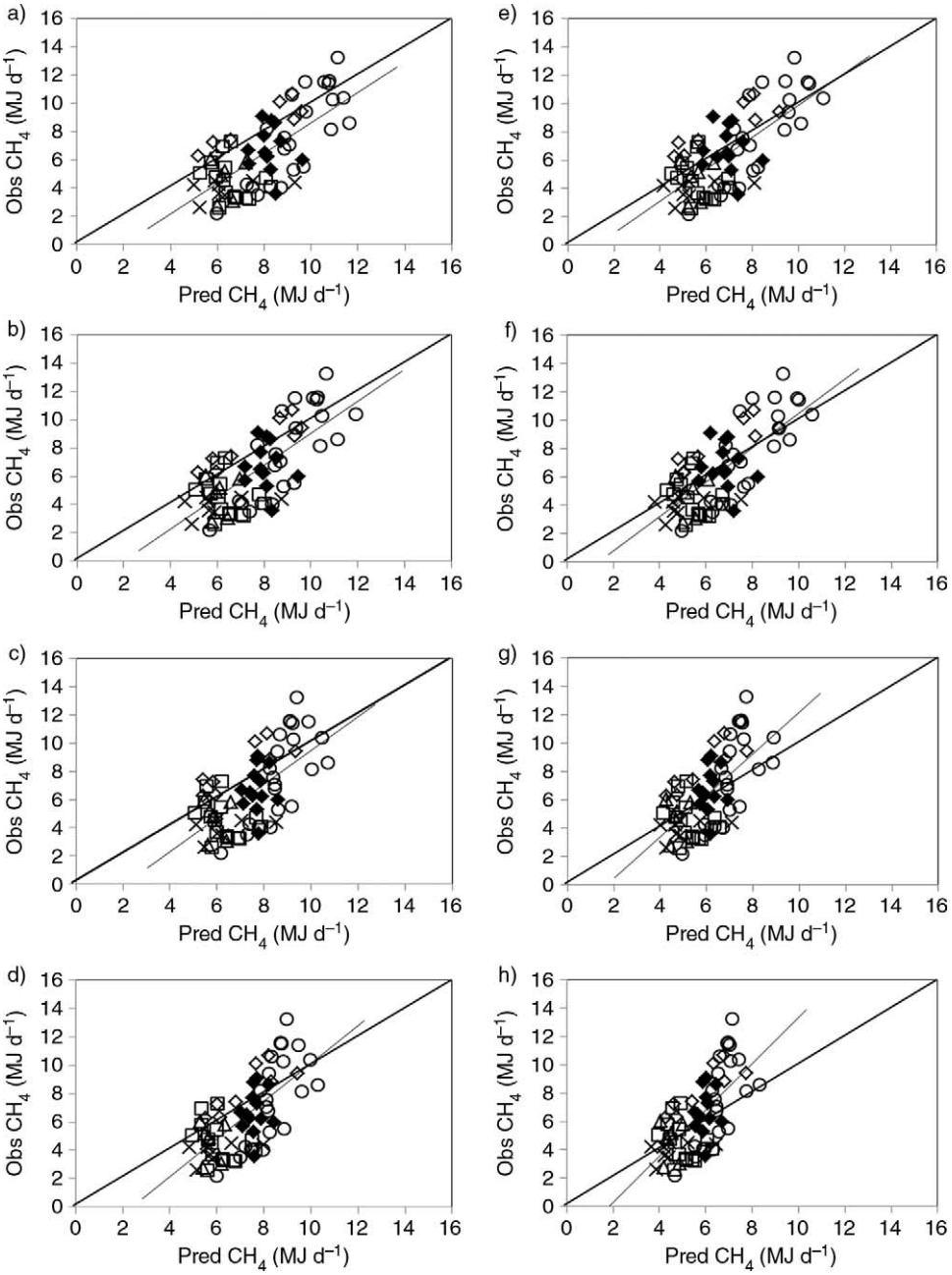

Fig. 2. Observed versus predicted CH_4 (MJ d^{-1}) where the predicted values are outputs from the Dijkstra model using the VFA stoichiometry of (a) Bannink et al. (2006), (b) Bannink et al. (2006) with Ellis et al. (2012), (c) Bannink et al. (2008), (d) Bannink et al. (2008) with Ellis et al. (2012), (e) Murphy et al. (1982), (f) Murphy et al. (1982) with Ellis et al. (2012), (g) Argyle and Baldwin (1988), (h) Argyle and Baldwin (1988) with Ellis et al. (2012), and where data are from Archibeque et al. (2006, 2007a, b, c) (◆, □, Δ), Beauchemin and McGinn (2005, 2006) (×, ◇) and Nkrumah et al. (2006) (○) ($n = 74$). The VFA stoichiometries are summarized in Table 1.

These mechanistic models have the potential to describe several of the fermentative and digestive processes which are not included in the empirical approaches, and allow predictions of CH_4 emissions in response to dietary changes that are more credible than empirical approaches as shown previously (Kebreab et al. 2008).

Monensin Stoichiometry

Consistent improvements in both RMSPE and CCC were obtained with application of the Ellis et al. (2012) monensin adjustment within the Bannink et al. (2006, 2008) and with the Murphy et al. (1982) stoichiometry. Predictions worsened with the Argyle and Baldwin

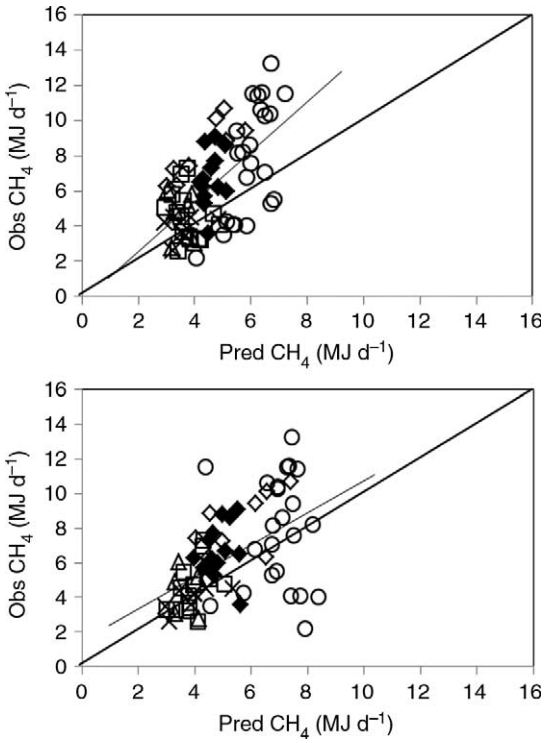

Fig. 3. Observed versus predicted CH_4 (MJ d^{-1}) where the predicted values are according to IPCC Tier-2 (2006) (top) and equation 10b by Ellis et al. (2007) (bottom) for feedlot beef cattle, and where the data are from Archibeque et al. (2006, 2007a, b, c) (◆, □, Δ), Beauchemin and McGinn (2005, 2006) (×, ◇) and Nkrumah et al. (2006) (○) ($n = 74$).

(1988) stoichiometry as the monensin adjustment further reduced CH_4 emission predictions that were already under-predicted. Until recently, no specific account of monensin feeding could be taken using empirical equations. However, Appuhamy et al. (2013) recently determined estimates of CH_4 (g d^{-1} and% GEI) change with monensin feeding for both dairy and beef cattle, which could tentatively be applied to empirical estimates. In the current study, application of such an estimate to the empirical equations would reduce the IPCC Tier 2 and the Ellis et al. (2007 Eq. 10b) predicted means, furthering the degree of under-prediction by these models and worsening the predictions. On average, across the database, predicted CH_4 (MJ d^{-1}) was reduced by 3.6% with inclusion of the monensin stoichiometry, where the average monensin dose for the database was 17.4 ± 8.8 mg kg DM^{-1}. This paper does not aim to prove or disprove a significant effect of monensin treatment on CH_4 emissions. In the rumen, more factors are interacting to determine CH_4 emissions than VFA stoichiometry alone, and monensin may have short- or long-lived effects on other aspects of rumen fermentation. However, the effect of monensin on rumen VFA stoichiometry is well documented, seems to persist over time (Guan et al. 2006), and is specifically associated with an increase in propionate production in the rumen (McGuffey et al. 2001). A shift in fermentation patterns towards more propionate production is associated with a reduction in CH_4 emissions (Ellis et al. 2008; Beauchemin et al. 2009). Based on changes in VFA stoichiometry alone it seems that CH_4 would be reduced by monensin.

Beauchemin et al. (2008), in a summary of the literature, found that the effect of monensin on CH_4 may be dose dependent. In that review, doses of less than 15 ppm monensin had no effect on CH_4 production (g d^{-1} or g kg DMI^{-1}) in dairy cows, doses of less than 20 ppm either had no effect or reduced total CH_4 (g d^{-1}, but not g kg DMI^{-1}) in dairy cows, and higher doses (24–35 ppm) reduced CH_4 production (g d^{-1} by 4–10% and g kg DMI^{-1} by 3–8%) in both beef cattle and dairy cows, with short-term decreases of up to 30% for both high and low forage diets. More recently, Appuhamy et al. (2013) demonstrated dose-dependent findings across both dairy and beef cattle. The predicted 3.6% reduction of CH_4 (MJ d^{-1}) with 18.6 mg monensin kg^{-1} DM in the current study is consistent with the findings of Beauchemin et al. (2008). Equations developed in Ellis et al. (2012) seem to capture at least part of the longer-term impact of monensin on the rumen fermentation pattern, as opposed to transient (larger) modifications that may occur in the rumen in the short term (e.g., effects on protozoa).

Variance Considerations

In general the RMSPE values presented here are high, and this is likely the result in part of using animal × treatment means from the test database [as did Kebreab et al. (2008)] as opposed to treatment means. There is merit in such an approach for challenging this mechanistic model, as additional variation in DMI and BW, digestibility and rumen pH force the model (or modeler) to find a solution for a more varied data set. Predictions based on treatment means will inherently be better, due to lower variation.

Within the Bannink line of stoichiometry, the mean CH_4 (MJ d^{-1}) and RMSPE were reduced and the percent of error from random sources was increased comparing the Bannink et al. (2006) pH-independent to the Bannink et al. (2008) pH-dependent stoichiometry. The CCC statistic, however, decreased slightly due to a lower P value despite C_b increasing slightly. Within the Murphy line of stoichiometry, the mean CH_4 (MJ d^{-1}) value was reduced to below the observed average and the RMSPE actually increased with the pH-dependent stoichiometry, with a slight increase in error due to deviation of the regression slope from unity. For the Murphy line of stoichiometry, the CCC statistic was also reduced with introduction of pH-dependence, as a flattening of the predictions occurred, resulting in a large v value (ratio of observed to predicted variance).

The loss in variance in predicted values due to incorporation of pH into the VFA stoichiometry was more severe in the Murphy line of stoichiometry compared with the Bannink line, given the same prediction of rumen pH, evident by the proportionally larger increase in the *v* statistic. Some of the flattening effect seen in both lines of stoichiometry could be attributed to a lack of variation in predicted pH (Fig. 1, discussed above), and perhaps better capture of observed variation in ruminal pH would lead to better CCC values for these pH-dependent stoichiometries. However, the effect of pH on the VFA profile is much more severe with the Argyle and Baldwin (1988) stoichiometry, with a linear relation with abrupt changes at pH 6.2 and 5.4, versus the sigmoidal relationship in the Bannink et al. (2008) stoichiometry. The pH-dependent stoichiometry of Argyle and Baldwin (1988) did reduce the average predicted CH_4 (MJ d^{-1}) to below the observed CH_4 (MJ d^{-1}) mean (Table 4), and although the basal CH_4 level is higher in the Bannink line, a similar reduction in the average predicted CH_4 mean occurred with the Bannink et al. (2008) pH-dependent stoichiometry without as great a loss in predicted variance.

With a tendency for under-prediction, the empirical equations used here for comparison had higher RMSPE and lower CCC values compared with the mechanistic approach (Table 4, Fig. 3). Empirical equations are valuable as they allow an easily obtainable estimate of CH_4 emissions with minimal input, but as the diet diverges from those included in the developmental database (even within the "high grain fed beef cattle" category), prediction worsens with little ability to improve or understand the background of the prediction error.

None of the stoichiometries or empirical equations were able to reproduce the level of observed variation (SD of the observed mean, 2.65 MJ d^{-1}). The highest predicted SD was 1.70 MJ d^{-1}, with the Bannink et al. (2006) stoichiometry (Table 4). Visually, a lower predicted variance level gives the impression of a "flat line" in the predicted versus observed plot. The scale shift factor within the CCC analysis, *v*, is a measure of this, being the ratio of observed to predicted variance. In Table 4, it is evident that especially within the Murphy line of stoichiometry, *v* becomes much larger with pH adjustments. While this is not as evident in the RMSPE values, it is evident in CCC analysis by producing a lower C_b and subsequent changes in the CCC value. In this respect, CCC analysis might be a better evaluation tool for data with a tendency for flat line predictions, as it picks up on this trend [discussed by Ellis et al. (2010)].

All VFA stoichiometries combined with the Dijkstra model had difficulty predicting very low CH_4 production values seen in the observed data, where CH_4 was 2–3 MJ d^{-1}, corresponding to less than 2% of GEI (Fig. 2). Although the Argyle and Baldwin (1988) and Argyle and Baldwin (1988) with the Ellis et al. (2012) monensin adjustment stoichiometries under-predicted the observed CH_4 (MJ d^{-1}) mean (Table 4), this was mainly due to under-prediction of higher observed CH_4 values (Fig. 2). The Murphy line of stoichiometry still over-predicted CH_4 values of 2–3 MJ d^{-1}, along with the rest of the stoichiometries. A problem evident by examination of the observed data is that CH_4 production values of less than 2% GEI were observed in individual animals on the same diets that produced CH_4 values of 3–5% GEI per day with other animals. This represents observed variation that the model is unable to explain. While values as low as 2–3% GE intake per day are observed with high-grain-fed beef cattle (e.g., Hales et al. 2012), all of the extremely low (<2%) values in the current database were from the Archibeque et al. (2006, 2007a, b, c) data, and some of this low-end variation may be an artefact of the short time period for which CH_4 was measured (6 h), and how that time period related to timing of the last meal. A more reliable comparison could have been made, had CH_4 been measured for 24 h. On the other hand, if the CH_4 treatment means are evaluated instead of individual animal data, much of this variation disappears, along with some of these extremely low CH_4 values. As is, the models seem unable to predict such low CH_4 production levels for the diets specified. This could indicate an inadequacy in the observed values, or that further improvements to the model, and/or the VFA stoichiometry are required to make it applicable to high concentrate beef cattle diets with extremely low CH_4 emission levels.

In summary, results of this study indicate that the Dijkstra model, prior to modification, was not suitable for use with finishing beef cattle fed high-grain diets, and that modifications to passage rate, volume and fiber degradation kinetics were required. Compared with a previous evaluation of the model using beef cattle data, significant improvements in CH_4 predictions and model functionality have been made. Post model modification, analysis of several VFA stoichiometry options revealed improvements in CH_4 (MJ d^{-1}) predictions (MSPE but not CCC) when the Bannink et al. (2006) VFA stoichiometry was replaced with the pH-dependent VFA stoichiometry of Bannink et al. (2008), but that replacement of Murphy et al. (1982) with Argyle and Baldwin (1988) reduced predicted variance, reduced CCC and increased RMSPE. Overall, Murphy et al. (1982) still produced the best predictions with the lowest RMSPE and highest CCC values. Improvements in both MSPE and CCC were obtained for most stoichiometries when the effect of monensin was included according to Ellis et al. (2012). In comparison with the Bannink approach based on dairy cattle data, the stoichiometries of Murphy et al. (1982) and Argyle and Baldwin (1988), based partially on beef cattle data, predicted lower mean CH_4 (MJ d^{-1}) values. Results indicate that improvements have been made to the model, to VFA stoichiometry and the capacity to predict CH_4, but that results remain unsatisfying, and further work on VFA stoichiometry and representation

of rumen function and pH for beef cattle fed high-grain diets is required.

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