BIOGAS PURIFICATION AND USE AS VEHICLE FUEL IN RURAL AREAS

Ruiz, B.[a], Gómez, P.[a], Giralda, R.[a], Carreras, N.[b], Rodríguez, M.[b], Ramos, J.L.[b], Morales, J.[c], Muñoz, S.[c], Torrente, M.[c], Pascual, A.[a]
[a]Ainia Technology Centre. Technology Park Valencia. Benjamin Franklin 5-11. 46980 Paterna (Valencia). Spain.
[b]Centre for research of Energy, Environment and Technology (CIEMAT). Av. Complutense 40. 28040 Madrid. Spain.
[c]Hera Amasa, S.A., Technology Park Vallès. Ed.A2 Paletes 6. 08290 Cerdanyola del Vallès (Barcelona). Spain.

ABSTRACT: The aim of the study is to demonstrate the technical feasibility of biogas purification and use as vehicle fuel in rural areas from alternative biomasses. A preliminary economic balance will also be estimated. The study will be carried out in the facilities of the anaerobic digestion plant installed in Farm San Ramón (Requena, Valencia, Spain). A biogas purification pilot plant, based on chemical scrubbing with amines, has been installed next to the plant and connected to the biogas output. The biomethane obtained will be tested in a vehicle. During the operation of the pilot plant data will be obtained on amine consumption, energy demands, quality of purified biogas, efficiency of the purification process and performance of the demonstration vehicle. Several parameters and indexes have been defined for the assessment of the purification yield and the performance of the demonstration vehicle. Alternative biomasses related to main Spanish crop residues have been identified and quantified.
Keywords: absorption, agricultural biogas plant, biogas, alternative fuel vehicle, biomethane, gas cleaning.

1 INTRODUCTION

Anaerobic digestion is a suitable process for the treatment of organic waste. It offers significant advantages over other forms of waste treatment including: appropriateness for treating wet wastes of less than 40% dry matter, more effective pathogen reduction, fertilizer production (digestate) and carbon neutral energy production in the form of biogas ([1]).

Anaerobic digestion has been successfully applied to farm waste, agricultural waste, food waste, etc. Nevertheless, since these resources can pose some difficulties (local availability, seasonality, presence of inhibitors), there is a demand for **new biomasses** that can be used in areas where small amounts of waste are available.

The products of anaerobic digestion process are biogas and digestate. Biogas average composition is 60% methane and 40% carbon dioxide, and traces of other gases such as hydrogen sulphide and other sulphide compounds, siloxanes, and aromatic and halogenated compounds ([2]). Biogas can be purified to obtain a gas similar to natural gas in composition and applications. This gas is called **biomethane**, and it has an average methane content of 97% ([3]). Since its composition is very similar to natural gas, these gases are fully interchangeable in their uses (gas grid, vehicle fuel, etc.).

There are several technologies that can be applied to biogas purification to biomethane quality. Among those, the main options are water scrubbing, chemical absorption (amines), pressure swing adsorption, membrane separation and cryogenic separation ([4]).

The objective of the research presented on this paper is to demonstrate the technical, economical and environmental feasibility of biogas purification and use of the resulting biomethane as vehicle fuel, from farm waste and alternative biomasses in rural areas of Spain.

2 MATERIALS AND METHODS

2.1 Alternative biomasses identification and quantification

The materials identified as alternative biomasses under Spanish conditions were algae, cereals, harvest residues, and industrial organic waste. Algae were not quantified since its production is still minority and limited to the experimental area. Industrial organic wastes were already quantified in the project PROBIOGAS ([5]). Thus, in this research, cereals, vegetables and other harvest residues were quantified with the base of harvest data of main Spanish crops. In particular, quantified residues corresponds to the harvest of cereals (barley, rye, maize, rice, sorghum, oat, triticale and wheat), vegetables (chard, garlic, artichoke, aubergine, courgette, pumpkin, artichoke thistle, onion, spring onion, cabbage, cauliflower, chicory, escarole, spinach, strawberry plant, lettuce, melon, turnip, cucumber, pepper, leek, radish, watermelon, tomato and carrot), industrial crops (cotton, sunflower and beet), tubers (potato) and legumes (broad bean, common bean, lentil, common vetch, pea and chickpea).

In order to estimate the quantities produced, official published data were taken from the Spanish Ministry of Agriculture (production data, [6]) and Spanish National Statistics Institute (surface data, [7]).

The quantities of alternative biomasses from plant origin located in Spain were calculated from available production data and taking into account: crop surface and yield distribution by “comarcas" (administrative division comprising a certain number of municipalities), crop production by provinces, specific ratio residue/product (obtained from different authors and studies), accessibility ratio (0.8) and availability ratio (0.25).

2.2 Batch anaerobic digestion tests

Batch anaerobic digestion tests were carried out in order to measure the biogas maximum potential (BMP) of the identified alternative biomasses.

The alternative biomasses tested were three species of microalgae, cereals (different varieties of barley, oat, wheat, triticale, rye, sorghum, maize and sunflower), harvest residues (straw, horticultural waste), industrial vegetable processing waste (bagasses, husks, filtration cakes), and farm wastes (pig slurry, sheep manure, poultry manure).

The BMP tests were carried out in 2L glass bottles placed in Binder® incubators at 38ºC and connected to Ritter Milligascounters® MGC-1 to measure biogas flow. Biogas composition was analyzed by means of an Awite® serie 6 gas analyzer (infrared sensors to measure methane, carbon dioxide and oxygen; electrochemical sensors for the measurement of hydrogen sulphide and hydrogen).

As inoculum, the digested material of an industrial running biogas plant was used. The chemical composition (total and volatile solids) of substrate, inoculum and digestates was determined in order to calculate biodegradability in terms of volatile solids elimination.

2.3 Semi-continuous anaerobic co-digestion tests

Semi-continuous anaerobic co-digestion tests were carried out to assess the performance of the co-digestion of farm organic waste and alternative biomasses. During start-up phase, digesters were fed with different mixtures of cow manure and co-substrates (wheat straw, barley straw, oat hay, rye straw). The organic loading rate (OLR) of digesters was progressively increased from 0.5 until 3.0 $kgVS \cdot m^{-3} \cdot d^{-1}$. At the same time, percentage of co-substrate in the mixture was adjusted until achieving a stable process. The steady state operating conditions are shown in Table I.

Table I: Steady state operating conditions of semi-continuous digesters.

	Cow Manure (%)	Substrate (%)	Substrate	OLR ($kg_{VS} \cdot m^{-3} \cdot d^{-1}$)
M1	66	34	Wheat straw	3.0
M2	73	27	Oat hay	3.0
M3	67	33	Barley straw	3.0
M4	72	28	Rye straw	3.0

The anaerobic digestion tests were carried out in jacketed continuous stirred tank reactors (CSTR) of 36L capacity (30L working volume) at 38ºC. The digesters were manually fed once a day with the selected mixture and organic loading rate (OLR).

Digestate was analyzed weekly for determination of total solids (TS), volatile solids (VS), pH, ammonia, volatile fatty acids (VFA) and alkalinity ratio. Analyses were conducted following standard methods ([8]).

Biogas was measured by means of Ritter Milligascounters®, and biogas composition was analyzed in an Awite® Serie 6 gas analyzer.

2.4 Biogas purification pilot plant

The biogas purification pilot plant was installed in the facilities of the anaerobic digestion plant of Farm San Ramón (Requena, Valencia, Spain). This plant uses cow manure from the farm and vegetal co-substrates as feedstocks (35,000 t/year). The biogas is currently used in a CHP engine of 500 kW installed electric power. A biogas purification pilot plant based on chemical scrubbing with amines has been installed next to the plant and connected to the biogas output. The pilot plant has a treatment capacity of 50 Nm^3/h.

The biogas purification takes place in several steps: 1) Pressurization, to overcome the pressure losses across the process; 2) Cooling, to achieve optimal temperature for the chemical reactions involved in biogas purification; 3) H_2S removal by adsorption on active coal; 4) CO_2 absorption with amines aqueous solution; 5) Biomethane drying; 6) Odorization by tetrahydrothiophen (THT) addition; 7) Amine regeneration (stripping, reboiling and condensation); 8) Biomethane compression, drying and filtering; 9) Storage (capacity 480 Nm^3). This technology (chemical scrubbing) is present in only 11% of the biogas purification plants worldwide. None of these plants treat the biogas produced in an agro-industrial biogas plant.

3 RESULTS AND DISCUSSION

3.1 Alternative biomasses

Table II shows the estimated quantities of alternative biomasses derived from data of main crops harvested in Spain for the different regions (Autonomous Communities). More than a half of the estimated alternative biomasses are located in three regions: Castilla y León, Andalucía and Castilla-la Mancha. That means north-western-central, south-eastern-central and south of Spain. The estimated amounts of these regions are 2.6 million of tonnes per year (56% of the total amount).

Table II: Estimated quantities of alternative biomasses from crop residues considering different Autonomous Communities (AC):

AC	residue $t \cdot year^{-1}$	%
Andalucía (AND)	949,882	19.9
Aragón (ARA)	437,519	9.2
Asturias (AST)	5,637	0.1
Baleares (BAL)	42,393	0.9
Cantabria (CAN)	2,173	0.0
Castilla-La Mancha (CLM)	554,580	11.6
Castilla León (CYL)	1,182,918	24.8
Cataluña (CAT)	207,224	4.3
Comunidad Valenciana (CV)	176,419	3.7
Extremadura (EXT)	324,107	6.8
Galicia (GAL)	112,133	2.3
Islas Canarias (ICA)	33,176	0.7
La Rioja (RIO)	57,431	1.2
Madrid (MAD)	63,464	1.3
Murcia (MUR)	361,740	7.6
Navarra (NAV)	201,139	4.2
País Vasco (VAS)	66,301	1.4
Spain (Total)	4,778,236	100.0

On one hand, it is important to remark that main substrates corresponds to residues from vegetables and cereals (88% of the total Spanish amount, see Table III).

Table III: Estimated quantities of alternative biomasses considering main crop groups.

Crop group	residue ($t \cdot year^{-1}$)	%
Cereals	2,638,750	55.2
Vegetables	1,579,249	33.1
Industrial crops	438,512	9.2
Tubers	108,292	2.3
Legumes	13,433	0.3

Vegetable residues are mainly located in Andalucía, Murcia and Comunidad Valenciana and cereals harvest residues are mostly located in Castilla y León, Aragón and Castilla-La Mancha (see Table IV). Those regions concentrate between 63% and 94% of the total quantities for each group.

On the other hand, previous studies ([9]) indicate that there is a deficit of co-substrates in different locations of Spain. More than 100 “comarcas” have, as percentage of available co-substrates, less than 5% from the total amount of organic agro-industrial waste. Among them, 24% is located in Castilla y León, 16% in Aragón, 14% in Extremadura, 12% in Castilla-La Mancha and 10% in Cataluña.

Table IV: Autonomous communities (AC) where residues are concentrated (percentage of the total quantity from each crop group).

	1st AC	%	2nd AC	%	3rd AC	%
Cereals	CYL	34	ARA	15	CLM	15
Vegetables	AND	31	MUR	22	CV	10
Ind. crops	CYL	44	AND	40	CLM	9
Tubers	CYL	36	AND	21	GAL	13
Legumes	CYL	46	AND	22	CLM	12

Due to this situation, alternative biomasses could be a good solution in order to increase the quantity of co-substrates for biogas production in those areas. Mainly, “comarcas” located in Castilla y León, Aragón and Castilla-La Mancha could have a higher benefit from alternative biomasses sources.

3.2 BMP tests

Methane yield was between 249-375 NL_{CH4}/kg_{VS} for microalgae, 219-452 NL_{CH4}/kg_{VS} for crops, 212-397 NL_{CH4}/kg_{VS} for harvest residues, 283-418 NL_{CH4}/kg_{VS} for industrial organic waste and 140-432 NL_{CH4}/kg_{VS} for farm organic waste. Figure 1 shows the average results of each category or material group. The highest methane yield was observed for crops, followed by industrial organic waste, farm organic waste, algae and harvest residues.

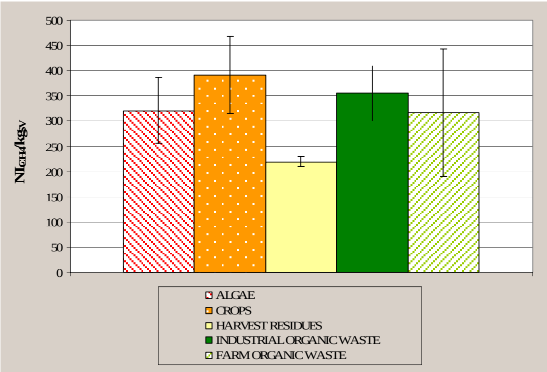

Figure 1: Methane yield of each material group.

Considering maximum slope (Figure 2), industrial organic waste showed the highest mean value, follow by crops, microalgae, farm organic waste and harvest residues.

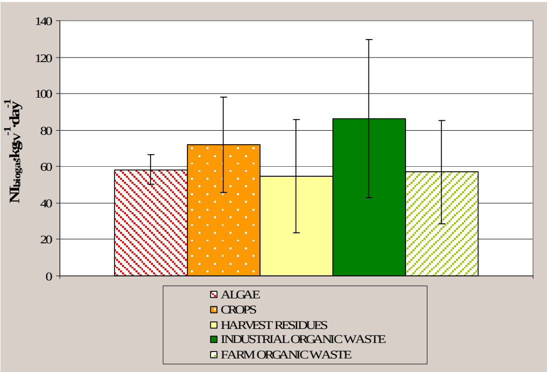

Figure 2: Maximum slope considering material group

3.3 Semi-continuous anaerobic digestion tests

Figure 3 shows biogas productivity in terms of volume of digester (a) and kilogram of volatile solid added (b). Mixture 4 (M4 – 72% cow manure and 28% rye straw, wet basis) showed the best result in terms of biogas yield per m3 digester and per kgVS added.

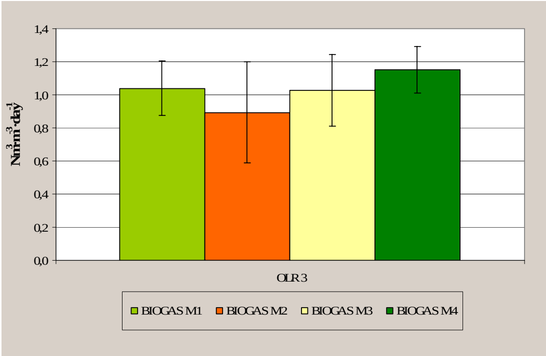

Figure 3a: Biogas yield per volume unit of digester

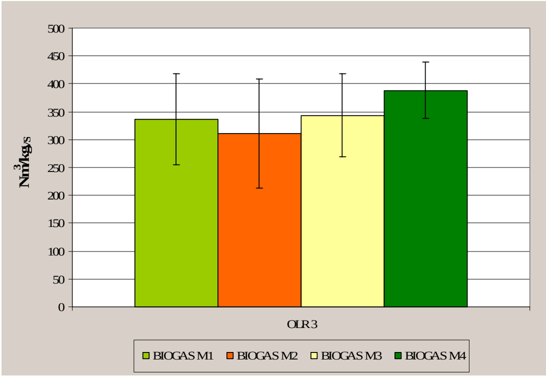

Figure 3b: Biogas yield per mass unit of volatile solid

Biogas from all mixtures had similar methane content (44-47%). Hydrogen sulphide in biogas varied between 22 and 435 ppm. M2 and M4 generated a biogas with higher H_2S content, and digestates with higher ammonia concentration. Cow manure used for these mixtures was from the same origin but different set. That situation could have an influence on H_2S composition of the biogas and ammonia content of the digestate.

Anaerobic codigestion of all mixtures at OLR 3 run stable according to parameters like alkalinity ratio (<0.4), volatile fatty acids (<275 mg/kg) and H_2 concentration in biogas (<200 ppm).

Considering semi-continuous trials results, the percentage of crops or straw in the mixture with cow manure should be below 30% (in terms of fresh matter). The loss of alkalinity seems to be the main cause of that instability when co-substrates’ percentage in the mixture is higher than 30%.

3.4 Biogas purification and use

The following yields will be calculated for the biogas purification process:

- H_2S removal: $([H_2S]_{in}-[H_2S]_{out})/[H_2S]_{in}$
- CO_2 removal: $([CO_2]_{in}-[CO_2]_{out})/[CO_2]_{in}$
- CH_4 enrichment: $([CH_4]_{out}-[CH_4]_{in})/[H_2S]_{in}$
- Active coal consumption: AC(kg)/biomethane obtained (Nm^3) and AC(kg)/H_2S removed (g)
- Amine consumption: amine(L)/biomethane obtained (Nm^3) and amine(L)/CO_2 removed (kg)

- Energy consumption: energy consumed (kWh)/biomethane obtained (Nm^3)
- Energy balance: energy consumed (kWh)/energy content of the biomethane produced (kWh)

The biomethane obtained will be used in a vehicle used for several tasks inside the farm. During the operation of the pilot plant, data will be obtained on amine consumption, energy demands, quality of purified biogas, efficiency of the purification process and performance of the demonstration vehicle.

Regarding the performance of the demonstration vehicle, the following parameters will be assessed:

- Fuel efficiency: biomethane consumed (Nm^3)/distance covered (km)
- CO_2 emissions: CO_2 emission (gCO_2)/distance covered (km)
- Vehicle autonomy: distance covered (km) with one refuelling

Within a few months, the first results on the yields of the purification process will be obtained.

4 CONCLUSIONS

- The alternative biomasses quantified are located mainly in Castilla y León, Andalucía and Castilla la Mancha. As main co-substrates, residues from vegetables and cereals have been identified. Those co-substrates could be a good solution in case of many comarcas of Spain with lack of co-substrates.
- Among the alternative biomasses tested (batch lab scale tests), crops showed the highest methane yield and industrial organic waste the highest speed of degradation.
- At pilot scale, digesters under semi-continuous feeding conditions were running stable at OLR 3 $kgVS \cdot m^{-3} \cdot d^{-1}$ with mixtures of cow manure with less than 30% of co-substrate. In particular, rye straw seems to be a better co-substrate than oat hay.
- The methane content of both digesters was around 44-47% of CH_4 and the H_2S concentration reached in some cases 435 ppm. This composition makes necessary a step of purification and upgrading for its use as vehicle fuel.

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7 LOGO SPACE

AGROBIOMET project is co-financed by:

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