

Research Article

Proposal Integral Use of Divi-Divi Fruits (*Caesalpinia Coriaria*) in The Scope: Oil Well Drilling, Fodder and Social Development

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Abstract

In this work there appear the potentialities of fruit and powder of divi-divi as: water-based drilling fluids (WBDF) environmentally friendly deflocculant, leguminous fodder for ruminants and sustainable jobs in farm communities, able to influence the primary forests protection. Tannins extract in the form of divi-divi fruit powder (*Caesalpinia coriaria*), contains 47.0 wt% of total tannins (hydrolyzable tannins plus condensed tannins) of which 30.0 wt% corresponds to hydrolyzable tannins. Divi-divi tannins in WBDF showed nine (9) times deflocculant efficiency than heavy metals commercial modified tannins. Moreover, commercial modified tannins do not improve their deflocculant efficiency with increased tannin content. Bromatological and structural analysis of fruits (wet base), they show it as a maintenance fodder: 5.33% w/w crude protein, 9.68 wt% moisture, 77.03 wt% nitrogen-free extract (NFE) (Weende Method), 11.38 wt% neutral detergent fiber (NDF) and 5.52 wt% acid detergent fiber (ADF) (Van Soest method). Social-productive production of 15 divi-divi tannins in artisanal way with help of rural community Boquerón, belonging to the municipality Pedro Maria Freites of Anzoátegui state, there served as developing socially productive pilot model that as well as beneficial at 245 families, whose raw material is conceived as non-wood forest products (NWFP), improve the sustainable utilization of NWFP in order to contribute to the wise management of the world's forests and to improve income generation and food security.

Keywords: *Divi-Divi Tannins; Deflocculant; Social-Environmental Development; Tannins Bromatology Analysis; Water-Based Drilling Fluids.*

Introduction

Divi-divi tree (*Caesalpinia coriaria* Jacq. Wild) is a native plant from Central and South America, adapted to the arid and semi-arid soils of dry forests. The pods have a size ranging from 3 to 6 cm long with an average weight of 4 grams; they are green color when they are not ripe yet, when ripe they are dark brown color and contain a higher percentage of tannins [1-3]. This species is very well adapted to tropical dry forests, in Venezuela dry forests are threatened (developing threat) by logging, excessive burning and pasture. According to the United Nations Organization for Agriculture and Food (FAO), Bolivarian Republic of Venezuela ranked 5th among the South American nations with the highest rates of deforestation. FAO 2015 report, among 1990 - 2005 attributes deforestation rate in 7 countries of South America to several factors [4,5] (Figure1).

FAO and Center for International Forestry Research (CIFOR) believe that one of the strategies with the highest degree of sustainability and social protection in order to reduce deforestation is the development of non-wood forest products (NWFP) [4]. Forests are vital for soil conservation, carbon sequestration, habitat protection and cycle water [4]. This is the case of divi-divi fruits that can be harvest wild and produced in agro-forestry systems and promote socio-environmental development in the farm communities surrounding the oil fields in Venezuela.

In the oil industry, one of the primary stages in the exploration of oil and gas fields is the oil drilling operation, whose goal is to find hydrocarbons (oil & gas) in the subsoil, facilitate their extraction safely through wells well built and maintained, in the shortest time

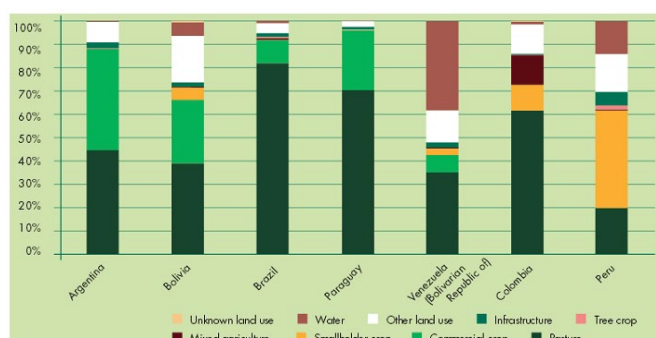


Figure 1: Proportion of deforestation attributed to various drivers in seven south american countries (1990–2005).

Source: De Sy et al., 2015 and state of the World's Forests 2015, FAO (2015).

and cost possible. Expenses of drilling operations represent 25 % total cost of exploitation of oil field [6]. Drilling fluids represent between 15 % and 18 % of the total cost of drilling an oil well [6,7] and must meet three essential requirements: i) simple to use, ii) not be expensive and iii) environmentally friendly or low environmental impact [6,8,9]. Oil & gas drilling activities consume annual tons of chemical additives to

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partially solve the problems associated with well drilling. The most commonly used additives in drilling fluids are: weighting materials, viscosifiers, deflocculates, dispersants fluid-loss control materials, surfactants, etc., of which the majorities are subject to environmental regulations [10].

Research proposal is oriented to the application of unmodified tannins extracted from the divi-divi fruits (NWFP) as a natural deflocculating additive in water-based drilling fluids and to be a stimulus for farm community's development through the sustainable management (circular and solidarity economy) of agriculture and dry forests [11].

Materials and Methods

Evaluation of tannins obtained from divi-divi fruit as deflocculant additive in WBDF and animal nutrition was carried out through of four (4) stages implementation:

First stage: organoleptic, chemical, physical, bromatological and structural analyzes of divi-divi fruits and tannins.

Second stage: divi-divi tannins thinner efficiency determination.

Third stage: contemplates a change of scale up in the divi-divi fruits collection and processing for their application in drilling wells and divi-divi fibrous residues utilization as fodder.

First stage. Divi-divi tannins physical and chemical properties determination

Collection, pretreatment and processing of divi-divi fruits

Divi-divi fruits three (3.0) kg were weighed. Subsequently, it was dried in an oven at 50 °C for 24 hours and then acclimated to room temperature. Dry fruits 3.0 kilograms were ground into 250.0 g portions in a blender with average grind times between 10 -15 s. Then it was sieved to 200 mesh and 325 mesh (75 µm to 45 µm). Divi-divi powder obtained was dried in an oven at 50 °C ± 0.1 °C for 24 hours and placed in desiccator [12,13].

Tannins determination

Percentage (wt/wt) of hydrolysable tannins in the tannin extract of fruit powder was determined using the analytical procedure indicated in ISO 9648:1988 [14-16], modified as follows: replacements of other chemical reagents that meet the same analytic functions. Briefly, standard solutions of tannic acid solutions were prepared at different concentrations and then an absorbance calibration curve vs tannic acid concentration using an UV-Visible spectrophotometer at λ = 525 nm was constructed. Hydrolysable tannins concentration and tannic acid in sample solutions was determined by interpolating their absorbance into standard solutions curve. Total tannins determination was carried out by soxhlet extraction method with an (20:80) ethanol:water mixtures on the whole fruits with 6.0 wt% ± 0.1 wt% humidity.

Preparation of solutions

Tannic acid standard solution: tannic acid 1.0000 g, FeCl₃ 1.8000 g and NaOH, 4.1000 g were weighed with an appreciation ± 0.0001 g and dissolved in distilled water, taking it to 500 mL volumetric flask.

Set of tannic acid standard solutions: in 20 mL volumetric flask separately, 1.0 mL, 2.0 mL 3.0 mL 4.0 mL and 5.0 mL of tannic acid standard solution were placed. These solutions will have the following concentrations: 0.1; 0.2; 0.3; 0.4 and 0.5 mg tannic acid/mL.

Tannin sample solution: powder divi-divi tannins 1.0000 g was weighed and dissolved in distilled water, taking it to 500 mL volumetric flask. This solution is filtered w/Whatman grade 44 filter paper. Then an aliquot of 5.0 mL of the solution was taken and it is brought to

capacity with distilled water to a 20 mL volumetric flask.

Bromatological analysis (wet weight basis) according to Weende method

System of proximal analysis [17,18] is a set of laboratory determinations that aims to evaluate globally each group of nutrients contained in a food. Consists of the following determinations: dry matter at 105 °C, humidity, crude fat (ether extract), crude fiber, nitrogen-free extract (NFE), crude protein and nitrogen and ash.

Structural analysis (wet weight basis) according to the Van Soest method

Method is based on the fractionation of the crude protein with the help of a surfactant in neutral and acidic medium. Method of proximal analysis allows determining the components of the food cell wall [19,20], such as: neutral detergent fiber (NDF %), acid detergent fiber (ADF %) and lignin.

Second stage. Divi-divi tannins deflocculating efficiency evaluation

Thinner efficiency

Efficiency and performance of divi-divi tannins as deflocculant additive was determined in water-based bentonite fluids (WBDF), similar to those used in drilling operations. Four (4) formulations of bentonitic fluids were prepared by duplicate and with different concentrations of salts to induce the flocculated state. ISO 10416: 2008 standard indicates how the deflocculating capacity of thinner in drilling fluids is determined of relative manner [21]. Parameters related to plastic viscosity of resulting suspension were determined by directly placing a portion of the suspension into a Fann 35A viscometer. In this way, plastic viscosities (PV), yield points (YP) and gel strengths were determined both before and after aging at 150 °F (65.5 °C) and 350 °F (176.6 °C), respectively [21].

WBDF preparation with NaCl and without gypsum

In a recipient, an aliquot 350 mL clay suspension was prepared as described in the previous section, adding this time 1.75 g NaCl (ACS grade). Mixture was stirred for 3 min at 750 r/min and immediately after stirring stopped, an aliquot of 5.00 g of the deflocculant additive to be tested was added to the suspension which was further stirred for an additional minute. Alkalinity of each sample was adjusted by adding a NaOH solution (1 mL = 0.25 g NaOH, ACS grade) in order to reach a pH 9.5 (Table 1).

WBDF preparation with gypsum and NaCl excess

A laboratory barrel (1 barrel (bbl) is equivalent to 350 mL) with suspension of clay plus 5.00 g of gypsum (CaSO₄·2H₂O) and 4.00 g NaCl (ACS grade) was prepared by the above-described laboratory procedure. The mixture was stirred for 3 min at 750 rpm. Then, an aliquot of 8.00 g of tested deflocculant additive was added, stirring the mixture for an additional minute. Alkalinity of each sample was adjusted to 9.5 units of pH by adding a NaOH solution (1 mL = 0.25 g NaOH, ACS grade) (Table 1).

Divi-divi tannins thinner efficiency

Performance as a thinner was evaluated using the standard

Table 1: WBDF formulations without excess NaCl and with excess NaCl/gypsum.

| Components | UN | WBDF Formulations | | | |
|--|----|-------------------|-------|-------|-------|
| | | FA | FB | FC | FD |
| Pre-hydrated bentonite (28 wt%) | g | 98.00 | 98.00 | 98.00 | 98.00 |
| NaCl ACS grade 99 wt% | g | 1.75 | 1.75 | 4.00 | 4.00 |
| Gypsum (CaSO ₄ ·2H ₂ O) p.a 99 wt% | g | 0.00 | 0.00 | 5.00 | 5.00 |
| Commercial tannin | g | 5.00 | 0.00 | 8.00 | 0.00 |
| Divi-divi tannins | g | 0.00 | 5.00 | 0.00 | 8.00 |
| NaOH ACS grade (pH adjustment at 9.50) | mL | 2.00 | 2.00 | 3.00 | 4.00 |

method [21]. Thinning efficiency (E) was calculated and expressed as a percentage of performance of the tannins relative to the performance of commercial modified tannins.

$$e_m (\%) = e_r \cdot (p_m/p_r) \cdot 100 \quad (\text{Eq. 1})$$

Where E_s = efficiency of the sample, P_s = performance of the sample in some rheological variable (PV, YP and gel strength), E_r = efficiency of commercial or reference tannins, P_r = performance of the commercial or reference in some rheological variable (PV, YP and gel strength).

Third stage: Divi-divi tannins socio-productive production for application in drilling wells.

Divi-divi tannins artisan scale production was implemented through a socio-productive agreement with organized farm community of Boquerón town, pertaining to Freites municipality of Anzoátegui state. Boquerón area was selected for having existing divi-divi wild trees in dry forest and Santa Rosa and Orocuál oil fields proximity. Boquerón farm community has a population of 400 inhabitants gathered in 172 families with its members ranging in age from 0 to 89 years. It has a territorial extension of 3,277 ha with primary dry forests. Divi-divi fruits were ground and sieved at 100 μm , then tannins powder was placed in plastic bags with a capacity of 15.0 \pm 0.1 kg and placed in palettes. Fibrous residues that remain after sieving are packaged in plastic bags and labeled as bovine livestock fodder.

Results and Discussion

Tannins determination

Total tannins percentage was 47 wt% \pm 4 wt% and hydrolysable tannins reached 30.3 wt% of total tannins and by percentage difference, 14.7 wt% corresponds to condensed tannins. High content of hydrolysable tannins in the divi-divi will allow greater solubility in water and consequently a greater quantity of ionic species negatively charged within the WBDF, efficiently acting in the neutralization of the attractive loads of clay, promoting a deflocculated state.

Organoleptic, chemical and physical analyzes

Divi-divi tannins organoleptic characteristics are similar to standard tannic acid used. However, color, taste and smell are particular characteristics that depend on each vegetal species. Divi-divi tannins has a ochre color, which is lighter when compared to two of the best known commercial tannic extracts such as: mimosa (*Acacia meamsii* y *Acacia dealbata*) and quebracho (*Scinopsis balansae*) (Figure 2). Divi-divi tannins have a bitter and astringent taste, typical of tannic a substance that causes the gum to gather when it is bitten or tasted.

Divi-divi tannins 2 wt% solution is acid (pH 4.4), which is consistent with reported literature for mimosa tannins (pH 4.0 - 4.5) and quebracho (pH 4.3 - 4.5) [22,23]. Density of 0.650 \pm 0.001 g/mL was determined by pycnometry. This density value is within the same magnitude order of tannic densities reported for mimosa ($\rho = 0.501$ g/mL) and quebracho ($\rho = 0.514$ g/mL) [24]. Divi-divi tannins moisture percentage was determined by Karl Fisher method being found 7.69 wt% \pm 0.01 wt%. Moisture of divi-divi tannins is similar to quebracho tannin of 8.0 wt% and lower than that of mimosa tannin of 6.2 wt%. Soluble solids percentage was 65.0 wt% \pm 0.5 wt%, determined



Figure 2: Tannin colors of vegetal species: divi-divi, quebracho and mimosa.

gravimetrically by [25].

Bromatological and structural analyzes

Divi-divi fruits contains 90.32 wt% dry matter (DM), 5.33 wt% crude protein, 77.03 wt% nitrogen-free extract (NFE), 9.68 wt% moisture, 11.38 wt% neutral detergent fiber (NDF) and 5.52 wt% acid detergent fiber (ADF) (Tables 2 and 3). Although these nutritional values are not high when compared with cuji fruits nutritional values (*Acacia macracantha*) and high-quality fodder [26]. Therefore they are sufficient to consider it as alternative food source and then fibrous residues [27,28]. However, tannins or polyphenolic substances are considered as natural anti-nutritive substances [29-32], but depending on the type and concentration of tannins (hydrolyzables or condensed), the animal nutrition will not be affected, benefiting the health and productivity of animal [33-37]. Therefore, fibrous residues obtained after tannins separation will be enriched in nutritious substances and impoverished in tannins. They also have an anthelmintic effect [38]. These nutritional, antiparasitic and antioxidant properties of divi-divi fruits are also present in fibrous residues, which allow contributing when used as a supplementary food source for ruminants during the dry season.

Divi-divi tannins deflocculating efficiency determination

Divi-divi tannins showed a deflocculating efficiency, before and after the dynamic aging at 150 °F (65 °C) similar to commercial tannin (Figures 3 and 4). Divi-divi tannins deflocculating efficiency drastically improves after dynamic aging at 350 °F, reaching an efficiency of 9.2 times higher than the commercial. Clay sheets tendency s to aggregate and flocculate (edge-edge and face-edge) due to temperature effect is minimized by negative charges additional contribution of hydrolysable divi-divi tannins to system and by increase of solubility with temperature, causing the separation of clay particles by repulsion forces action [16].

Boquerón farm community socio-productive agreement

Tannins production socio-productive agreement through with

Table 2: Divi-divi fruits bromatological analysis (Weende method)

| Sample | DM (wt%) | Moisture (wt%) | Ash (wt%) | Crude protein (wt%) | Nitrogen free (wt%) | Crude fiber (wt%) | Crude fat (wt%) | NFE (wt%) |
|------------------|----------|----------------|-----------|---------------------|---------------------|-------------------|-----------------|-----------|
| Divi-divi fruits | 90.32 | 9.68 | 2.31 | 5.33 | 0.85 | 5.10 | 0.55 | 76.18 |

Table 3: Divi-divi fruits estructural analysis (Van Soest method)

| Sample | NDF (wt%) | ADF (wt%) | Lignin (wt%) | Cellulose (wt%) | Hemi-cellulose (wt%) | Ash (wt%) |
|------------------|-----------|-----------|--------------|-----------------|----------------------|-----------|
| Divi-divi fruits | 11.38 | 5.52 | 0.50 | 3.96 | 5.86 | 1.06 |

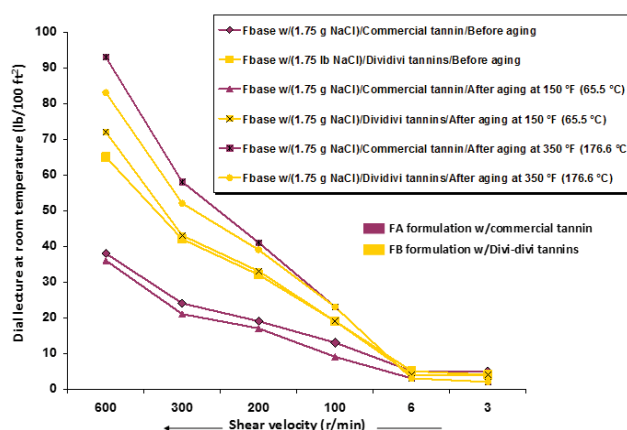


Figure 3: Rheological performances of FA and FB formulations at shear velocity different, before and after aging for 16 hour at 150 °F and 350 °F respectively.

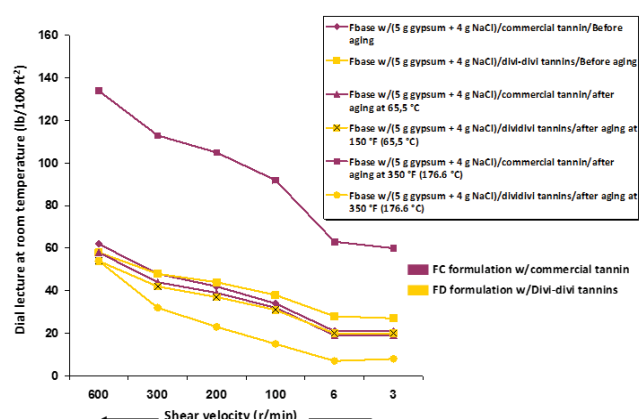


Figure 4: Rheological performances of FC and FD formulations at shear velocity different, before and after aging for 16 hour at 150 °F and 350 °F.

Boquerón farm community, 42,977 kg fruits obtained from wild trees belonging to the dry forests were collected. It was possible to obtain 15,000 kg of tannin powder and 27,977 kg of fibrous waste. Tannins powder was packed in low density polypropylene bags with a capacity of 15 kg. Pilot production of tannins benefited 245 rural families. Experience allowed to value divi-divi trees as a non-timber forest product (NWFP), which promotes the sustainability and protection of the surrounding primary forests.

Conclusions

1. Divi-divi fruits samples analyzed have 47.0 wt% total tannins (hydrolysable and condensed tannins) and 30.0 wt% are hydrolysable tannins.
2. Deflocculating efficiency of divi-divi tannins in water-based drilling fluids is 9 times greater reference commercial tannin efficiency
3. Divi-divi fruits and fibrous fiber nutritional values are suitable to be considered as sustenance folder.
4. Socio-environmental development pilot model for divi-divi tannins production benefited 245 families. Boquerón farm community now sees the divi-divi trees (*Caesalpinia coriaria*) as a non-wood forest product (NWFP). Now they are dry forests protectors.

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